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Studies of Flue Gas Desulfurization at Louisville Gas and Electric's Paddy's Run Station: Volume I. Carbide and Commercial Lime Testing

Radian Corp.
Austin, TX

Prepared for

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STUDIES OF FLUE GAS DESULFURIZATION AT LOUISVILLE GAS & ELECTRIC'S PADDY'S RUN STATION:

VOLUME I.
CARBIDE AND COMMERCIAL LIME TESTING

Prepared for:
ENVIRONMENTAL PROTECTION AGENCY
Industrial and Environmental Research Laboratory
Research Triangle Park, North Carolina 27711

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16. ABSTRACT

The report gives results of tests to determine the technical factors accounting for the success of the flue gas desulfurization (FGD) system at Louisville Gas and Electric Co.'s Paddy's Run Unit 6. (Between its start-up in the Spring of 1973 and the Fall of 1976, the Unit 6 FGD system logged almost 4000 hours of operation without any major process or mechanical problem.) Test results indicate that carbide lime (a waste by-product of acetylene manufacture using calcium carbide), used at Unit 6, contains oxidation inhibitors that prevent gypsum scaling in the FGD scrubber. Commercial lime testing without these inhibitors resulted in gypsum scaling. However, adding magnesium (3000 ppm in the slurry liquor) reduced sulfite dissolution in the scrubber, thereby reducing sulfite oxidation and allowing scale-free operation. Increasing the chloride level increased sulfite oxidation; an increase in magnesium addition offset the effects of higher chloride levels. Lime systems can be operated successfully with low reaction tank residence times because of the rapid dissolution of lime. The size of the reaction tank and the lime addition point affect the crystal structure of the scrubber waste solids.

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a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
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Flue Gases	Scaling	Stationary Sources	21B	11C
Desulfurization	Magnesium	Lime	07A,07D	
Carbides	Sulfites		07B	
Calcium Oxides	Chlorides			
Scrubbers	Wastes Crystal Structure		13I	14G 20B

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1.0 INTRODUCTION

Louisville Gas and Electric Company's (LG&E) Paddy's Run No. 6 flue gas desulfurization (FGD) system was one of the first commercial scale FGD units to be successfully operated in the U.S. Between its start-up in the spring of 1973 and the Fall of 1976, this unit logged close to 4000 hours of operation without encountering any major process or mechanical problems. Volume II of this report presents an analysis of the data collected on the system during this time period. Because of the demonstrated success of the Paddy's Run system, the Environmental Protection Agency sponsored a test program to determine the factors which account for the successful operation of this FGD system. At the time that this test program was conceived, a wide range of operating problems were being encountered in many FGD units. One of the more serious process problems was chemical scaling in the scrubber. One of the methods being investigated by many experimenters to avoid this problem was to operate the FGD system in such a manner that the slurry liquor remains subsaturated with respect to calcium sulfate dihydrate (gypsum). Recognizing this fact, the EPA conceived a program whose overall objectives were the following:

- To characterize the performance of the LG&E system in its "normal" operating mode, and determining the features which make it possible for this system to operate in a subsaturated gypsum mode.

- To conduct additional tests to
    - Simulate conditions more typical of those encountered in other lime-based systems
    - Determine the effects of changes in important process operating parameters

The intent of this program was to provide useful information which could be applied to other FGD systems. Ultimately, it was hoped that data from the successful operation at Paddy's Run could be extrapolated to other lime/limestone systems.

The overall organization of the program is shown in Figure 1-1. The operation of the unit was the responsibility of LG&E and their subcontractor, Combustion Engineering (CE). LG&E and CE were also responsible for some independent sludge disposal studies which were sponsored by the EPA.

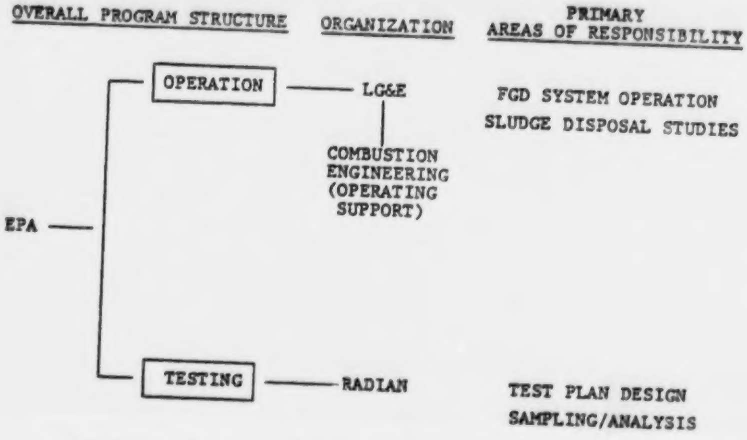

OVERALL PROGRAM STRUCTURE
ORGANIZATION
PRIMARY AREAS OF RESPONSIBILITY
EPA
OPERATION
LG&E
COMBUSTION ENGINEERING (OPERATING SUPPORT)
FGD SYSTEM OPERATION
SLUDGE DISPOSAL STUDIES
TESTING
RADIAN
TEST PLAN DESIGN
SAMPLING/ANALYSIS

Figure 1-1. Overall program organization.

Radian, as the independent test contractor, was responsible for

- the design of a specific test plan which would most effectively accomplish EPA's overall program objectives,
- the gathering and analysis of test data, and
- the documentation of test results.

This report, which satisfies the last of these responsibilities, provides an analysis of the results of the six-month LG&E test program. A brief overview of the program is presented in Section 2.0. This is followed by a detailed description of the Paddy's Run No. 6 system (Section 3.0), a discussion of the specific objectives of each test phase (Section 4.0), and a summary of the important program results (Section 5.0). Detailed discussions of the objectives, problems, and results of each test phase are presented in the appendices.

2.0 SUMMARY

Testing at Paddy's Run was conducted for a period of six months. During this time, both carbide lime and commercial lime were employed as alkaline additives. In addition, the impacts of high liquid phase magnesium (Mg^{++}) and chloride (Cl^-) concentrations and two different reaction tank configurations were tested. A summary of the significant program results is presented here.

Carbide *vs* Commercial Lime

Both carbide lime and commercial lime appear to be equally reactive in the Paddy's Run system since SO_2 removal efficiencies of about 75 percent were observed with both additives. Due to the relatively low L/G's and long slurry residence times inherent in the operation of the Paddy's Run marble-bed scrubber, a significant amount of the alkalinity required for SO_2 sorption was derived from solid phase calcium sulfite dissolution in the scrubber.

The existence of an oxidation inhibitor in the carbide lime appears to be the main difference between the two additives. With carbide lime, the oxidation fraction was generally less than 0.1. As expected at this low oxidation rate, all of the solid phase sulfate which formed was removed from the system as coprecipitated calcium sulfite-sulfate solids, and all system streams were subsaturated with respect to gypsum.

On the other hand, operation with commercial lime resulted in oxidation fractions of about 0.15. At this oxidation rate, the reaction tank liquor was still slightly subsaturated with respect to gypsum, so that all of the solid sulfate exiting the system was in the form of solid solution. However, the combination of 1) the higher scrubber feed liquor gypsum relative saturation caused by the increased oxidation and 2) the calcium solids dissolution which occurred on the marble beds, led to gypsum scaling in the scrubber. These scaling conditions could not be controlled at "base case" conditions, even when the system's maximum scrubber feed rate was employed.

Magnesium Addition

Major mechanical modifications would have been necessary to increase the system's L/G to the point where scaling could be controlled by this mechanism. For this reason, it was decided that magnesium should be added to the system to increase the scrubbing liquor's liquid phase alkalinity and reduce the requirement for the dissolution of alkaline solids.

There were two main effects of the magnesium addition. First, at magnesium concentrations above 120 mmole/liter (∿3000 ppm), the SO_2 removal efficiency was above 98 percent, and essentially no calcium solids were dissolved in the scrubber. Second, the addition of magnesium reduced the oxidation fraction. The combination of reduced calcium dissolution and lower oxidation reestablished conditions which were subsaturated with respect to gypsum in the scrubber.

The minimum magnesium levels which were found to be necessary to maintain system operability were in the 90 to 100 mmole/liter range. At this magnesium level, increases in both 1) calcium solids dissolution in the scrubber and 2) the oxidation rate were observed. The result was gypsum scale formation in the scrubber. This scale dissolved after the magnesium level was again increased.

While high magnesium concentrations were favorable from a scale control point of view, they also caused a solids handling problem. Magnesium concentrations above 180 mmole/liter resulted in the formation of solids with poor settling and dewatering characteristics. Safe operating limits between 120 and 160 mmole/liter were therefore indicated for the Paddy's Run system.

Obviously, the effect of magnesium on lime/limestone system operation will be somewhat site-specific. However, the results from this program demonstrated that an effective chemical mechanism does exist for enhancing the performance of a lime scrubber that is mechanically constrained. Both the SO_2 removal efficiency and the system's ability to operate without scaling were enhanced by magnesium addition.

The effects of magnesium addition shown in this program suggest a possible alternative to the mechanical cleaning of a scaled scrubber module. For example, it is conceivable that a lime scrubber which normally operates in the supersaturated mode with respect to gypsum could be cleaned of gypsum scale (e.g., which formed during a process upset) by a brief period of high magnesium operation.

Chloride Addition

Only a brief time period was available for testing the effect of chloride on system chemistry. Basically, an increase in chloride decreased the available scrubbing slurry liquid phase alkalinity. This led to calcium dissolution on the marble beds and, ultimately, to gypsum scaling. Increases in the Mg^{++}/Cl^- ratio restored operable conditions.

Reaction Tank Modifications

Two modifications to the Paddy's Run reaction tank system were tested. (Magnesium addition was required for these tests also). First, the hold tank draft tube of mixing well was eliminated. Normally, the scrubber effluent streams and the lime additive were mixed in the ∿13,000 liter vessel prior to entering the main reaction tank.

Material balance calculations indicated that, at base conditions, essentially all of the $Ca(OH)_2$ solids were dissolved and that the bulk of the calcium sulfite-sulfate solids were precipitated via nucleation and surface nucleation (rapid solids precipitation on the surface of existing crystals) in the draft tube. The bulk of the calcium sulfite-sulfate solids which were formed via this mechanism appeared in the form of rosettes (see Figure 2-1), a shape which is characteristic of the coprecipitated solids produced in most lime scrubbing systems. When the lime was added to the center of the main reaction tank, the effect of the draft tube was eliminated and precipitation began to occur by a more orderly crystal growth mechanism. In fact, operation without the draft tube and with lower magnesium concentrations produced platelets (see Figure 2-2) which are typical of the coprecipitated solids produced in limestone systems.

In a second reaction tank modification test, the lime addition point was returned to the draft tube, and the slurry residence time in the reaction tank was reduced from about 35 minutes to about 5 minutes. Operation in this mode led to formation of rosettes similar to those obtained during operation in the normal system configuration. This was expected since most of the precipitation had occurred in the draft tube even when the large reaction tank was employed. Higher oxidation fractions were encountered with the reduced volume, but the actual mechanism responsible for this effect could not be identified.

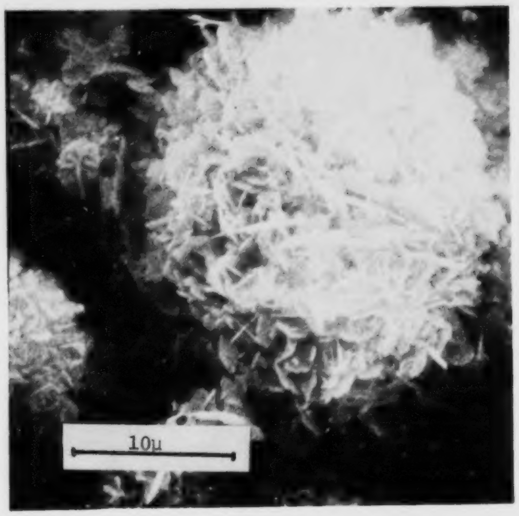


FIGURE 2-1 TYPICAL ROSETTE FORMED VIA SURFACE NUCLEATION IN LIME SYSTEM (JULY 5, 1977)

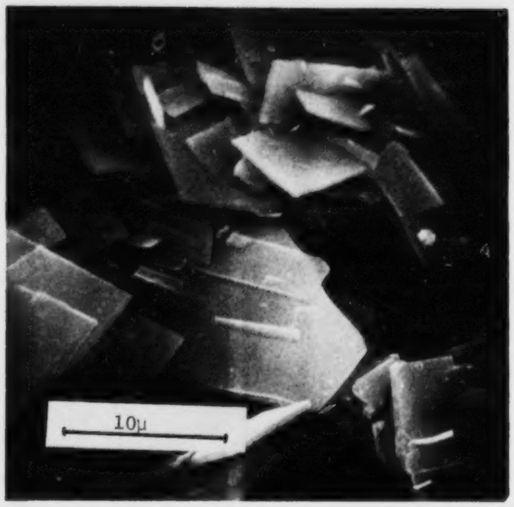


FIGURE 2-2 PLATELET STRUCTURE FORMED DURING "NO DRAFT TUBE" TESTING (AUGUST 8, 1977)

The hold tank modification tests showed that differences in product crystal structure can be induced in a lime system. It was also shown that the dominant precipitation mechanism and the resulting sludge particle size can have a major impact on solid waste characteristics (e.g., settling rate and settled density). Unfortunately, sufficient time was not available for a more complete study of the impact of system operation on sludge characteristics.

3.0 SYSTEM DESCRIPTION

The overall arrangement of the scrubbing system and its relationship to the No. 6 boiler at Paddy's Run is shown in Figure 3-1. Two scrubber modules operate in parallel at full load with a common slurry circulation system. Although the test boiler is rated at 65 MW, each module is designed to handle the flue gas equivalent of about 35-40 MW. This rating discrepancy is caused by the fact that the No. 6 boiler is an old boiler which has a high excess air ratio and a high preheater air leakage rate (its overall heat rate is about 3300 kcal/kWh [13,000$^+$ Btu/kWh]). During the EPA test program the boiler was operated at half load and only one scrubber module was used at a time.

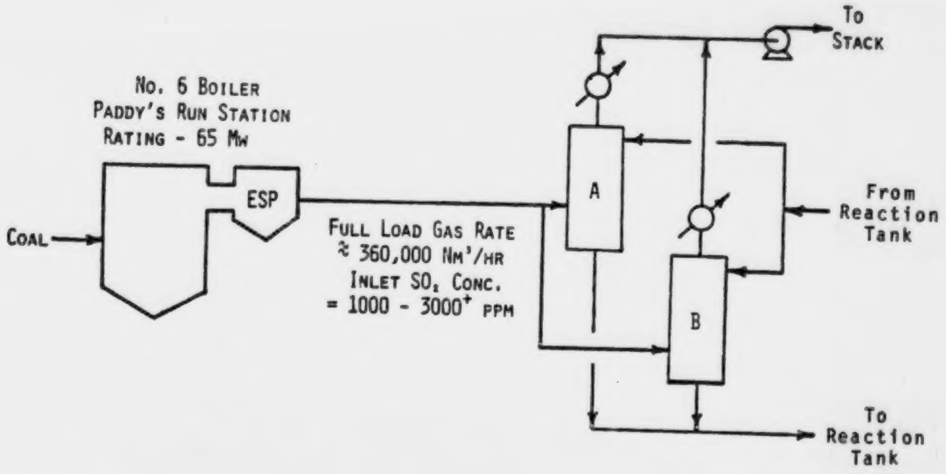
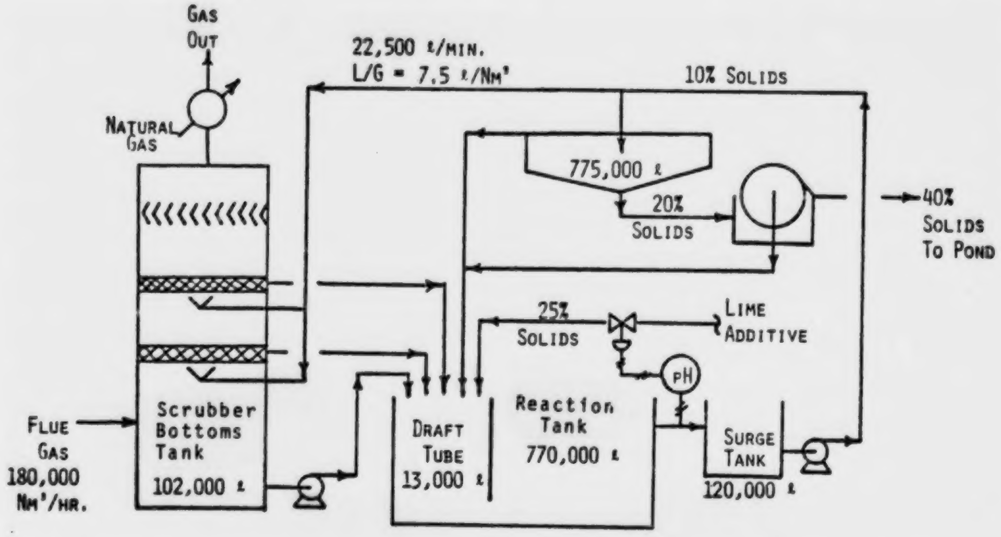

No. 6 Boiler
Paddy's Run Station
Rating - 65 Mw
Coal
ESP
Full Load Gas Rate
≈ 360,000 Nm³/hr
Inlet SO₂ Conc.
= 1000 - 3000⁺ ppm
A
B
To Stack
From Reaction Tank
To Reaction Tank

Figure 3-1. Paddy's Run scrubber tie-ins to the No. 6 boiler.

The major features of the FGD unit itself are shown in Figure 3-2. Basically, each scrubber module contains two marble beds in series followed by two banks of chevron mist eliminators.

The scrubbing liquor is introduced to the scrubber through spray nozzles located below each bed. The scrubber effluent liquid streams consist of the overflow liquors from the two marble beds as well as the scrubber bottoms liquor. Approximately 7 cm. (3 in.) of marbles are contained on each bed. The downcomer weirs are of such a height that the active gas-liquid contact zone on each bed is about 25 cm. (10 in.).



Gas Out
Natural Gas
22,500 ℓ/min.
L/G = 7.5 ℓ/Nm³
10% Solids
775,000 ℓ
20% Solids
40% Solids To Pond
25% Solids
Lime Additive
pH
Flue Gas 180,000 Nm³/hr.
Scrubber Bottoms Tank 102,000 ℓ
Draft Tube 13,000 ℓ
Reaction Tank 770,000 ℓ
Surge Tank 120,000 ℓ

Figure 3-2. Simplified flow diagram - Paddy's Run No. 6 FGD System.

The relative flow rates of the three scrubber effluent liquor streams are as follows. Roughly half of the feed liquor leaves the scrubber through the lower bed drains. An additional one-third of the feed liquor exits the scrubber through the upper bed drains. The remaining one-sixth of the scrubber feed liquor leaves the scrubber via the scrubber bottoms.

A unique feature of this system is the so-called draft tube, which is actually a small, well-mixed, bottomless tank into which the three scrubber effluent streams, the clarifier overflow liquor and the lime additive slurry flow before they enter the main reaction tank. The effective residence time of the draft tube is about 30 seconds whereas the residence times of the main hold tank and surge tank are about 35 and 5 minutes, respectively (all of these residence time figures are for half-load conditions). The residence time of the liquor on the beds averages about 30 seconds. The normal scrubber L/G is about 7.5 ℓ/Nm^3 (56 gal/scf).

The carbide lime used in the system is purchased from a local acetylene manufacturer. Commercial lime and coke are heated to form calcium carbide which upon reacting with water yields acetylene and lime. This regenerated lime contains some impurities and is referred to as carbide lime. The carbide lime additive is stored as a 25 percent slurry in an additive tank and is fed to the draft tube on pH demand. The pH set point of the hold tank effluent is generally 8.

The surge tank effluent serves as the scrubber feed stream. In addition, a portion of this stream is routed to the clarifier to maintain a circulating slurry solids level of 10 weight percent. The clarifier underflow (about 20% solids) is sent to a set of two vacuum filters which produce a filter cake containing 35-40 weight percent solids.

System makeup water comes from four sources: 1) mist eliminator wash water, 2) additive slurry, 3) turning vane spray wash water, and 4) seal water for pumps and mixers. The mist eliminator and turning vane spray washes are intermittent while seal water and the lime slurry are continuous makeup water sources.

4.0 PROGRAM OBJECTIVES

The overall objective of this test program was to determine quantitatively the reasons for the operating success of the Paddy's Run System. This unit had not experienced problems such as chemical scaling or mist eliminator pluggage which have been associated with many other lime and limestone SO_2 scrubbing systems. One important aspect related to this trouble free operation is the system's ability to operate subsaturated with respect to gypsum. This permits the system to operate without gypsum scaling problems.

It has been established that subsaturated conditions are related to sulfate coprecipitation with calcium sulfite. Laboratory studies have verified the formation of calcium sulfite-sulfate hemihydrate solid solution (1). These studies indicate that sulfate can be incorporated into the calcium sulfite lattice to a maximum sulfate to total sulfur ratio of about 0.16. In addition, the sulfate/total sulfur ratio in the solids is directly related to the gypsum relative saturation in the liquor. As long as the sulfate production rate does not exceed the rate at which sulfate can be incorporated into the sulfite lattice, the liquor from which the solids precipitate will remain subsaturated with respect to gypsum. Scaling is therefore not a problem in a liquor which is subsaturated with respect to gypsum.

There were several areas of interest regarding operation in the subsaturated mode. The primary area is the oxidation rate of sulfite to sulfate. System parameters which were thought to impact the oxidation rate or otherwise influence the subsaturated mode of operation included additive type (carbide lime *versus* other additives), reaction tank configuration, and soluble ion concentrations. It was anticipated that studies involving these parameters would yield insight into the question of why subsaturated gypsum operation is possible at Paddy's Run.

To fulfill the overall program objectives, four test phases were originally outlined:

Phase I - Carbide Lime Testing
Phase II - Commercial Lime Testing
Phase III - Hold Tank Modification Testing
Phase IV - Chloride/MgO Testing

The objectives of each of these test phases are discussed below.

Phase I - Carbide Lime Testing

The initial phase of testing involved characterizing the LG&E Paddy's Run No. 6 flue gas desulfurization system as it normally operates. This included the use of carbide lime as the additive.

As part of this test phase, steady-state operating conditions were established and key process performance parameters were monitored. Important system parameters measured included gas and liquid phase flows, temperatures, pressures and compositions; solid phase flows and compositions; and system liquid levels. These performance data were then used as a basis for the calculation of SO_2 removal rates, sulfite/sulfate precipitation rates, sulfite oxidation rates, and lime utilization efficiencies. Also, the results of this test phase served as "base case" conditions for purposes of comparison with subsequent test results.

Phase II - Commercial Lime Testing

The second phase of testing was performed using commercial lime as the alkaline additive rather than carbide lime. The major goal of this phase was to identify differences in operation which might be caused by the change in the source of the lime additive. Particular attention was given to monitoring oxidation rate effects. Prior to the start of this program, it had been hypothesized that carbide lime might contain an oxidation inhibitor which caused the system's oxidation rate to remain low.

All subsequent tests were conducted using commercial lime as the additive.

Phase III - Hold Tank Modifications

Lime systems have the advantage of a very rapid additive dissolution rate. Taking only this factor into account, high lime utilization efficiencies should be attainable even when very short reaction tank residence times are maintained. In practice, the minimum hold tank size in a lime system tends to be limited not by the kinetics of additive dissolution but rather by a complex set of factors which control the rates of precipitation of calcium sulfite and sulfate in the hold tank. As the reaction tank size is decreased, the realitive saturations of calcium sulfite and sulfate in the liquid phase will tend to increase (assuming that no other key system changes are made). In the limit, a decrease in hold tank size may lead to scaling if critical supersaturations of calcium sulfite and sulfate are exceeded in any part of the system. In one portion of this test phase, the reaction tank residence time was reduced to study the impact of this change upon the performance of the system.

A mechanical feature of LG&E's Paddy's Run FGD unit, which is unique to that particular system, is the draft tube or mixing well. It has been suggested that one of the keys to the success of the LG&E system is associated with the operation of this draft tube. This hypothesis was tested in a second reaction tank modification test which considered eliminating the effect of the draft tube. This was accomplished by changing the lime addition point from the draft tube to the reaction tank.

Phase IV - Chloride/MgO Testing

The final phase involved testing the effects of chloride and magnesium levels on subsaturated gypsum operation. It had been reported that increased chloride ion concentrations may decrease the amount of sulfate which can be purged from the system as a solid solution with calcium sulfite. Indications that increasing magnesium concentrations enhance the coprecipitation of calcium sulfate with calcium sulfite have also been reported. Supporting evidence for these claims was not found in recent laboratory studies by Jones (1); however, measurements of these effects in an actual operating system were desired during this test phase.

All of the major tests outlined for each test phase were conducted during the test program. However, due to differences encountered between commercial and carbide lime operation, the order of the tests had to be changed somewhat. As is discussed in the results section, operation with commercial lime led to scaling in the scrubber. Therefore, magnesium addition was employed to eliminate the scaling conditions prior to the hold tank modifications test phase. Consequently, the test phases were renumbered as shown below:

Phase I - Carbide Lime Testing
Phase II - Commercial Lime Testing
Phase III - MgO Addition Testing
Phase IV - Hold Tank Modifications
Phase V - Chloride Addition Testing

Magnesium addition was necessary throughout the last three test phases to maintain system operability.

5.0 TEST RESULTS

This section presents an overall summary of the results generated during the test program. More detailed discussions of the results obtained during each individual test phase are provided in Appendices A through E. These same results are presented here in a manner which facilitates comparison of the effects observed in different test phases.

Phase I - Carbide Lime Testing

Phase I was conducted over a six week period from mid-November through December, 1976. During this period, the operation of the unit was consistent with standard operating procedures observed previously. Data from Phase I are presented in Figures 5-1, 5-2, 5-3, and 5-4.

From Figure 5-1 it can be seen that, according to the on-line DuPont analyzer, the SO_2 removals which were observed during Phase I varied from about 75 to 83 percent. Wet test methods of these removal figures gave results which were about 5 percent lower.

Key scrubbing slurry properties are plotted in Figure 5-2. The scrubber feed pH was normally 8.0 while the lower bed downcomer pH was in the 4.5-5 range. The L/G during this operating period was about 7.5 ℓ/Nm^3.

The concentrations of important dissolved ions which were measured in the system during Phase I are plotted in Figure 5-3. A significant point to be noted here is the fact that the calcium level increased by about 50 to 70 percent across the scrubber due to the dissolution of solids in the low pH downcomer liquor. Note that the $SO_4^=$ level also increased across the scrubber, but only by about 20 to 40 percent.

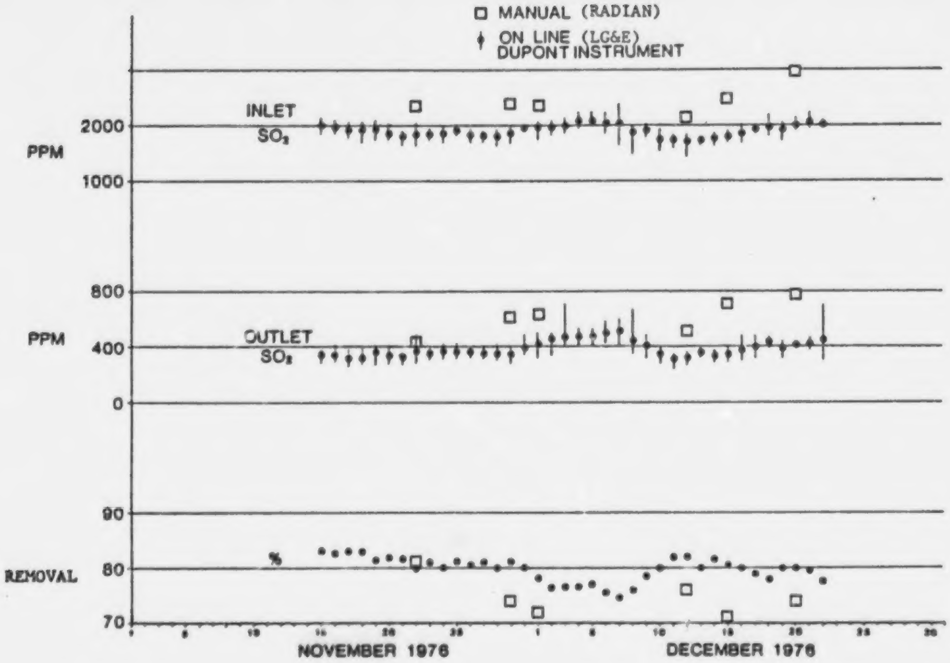
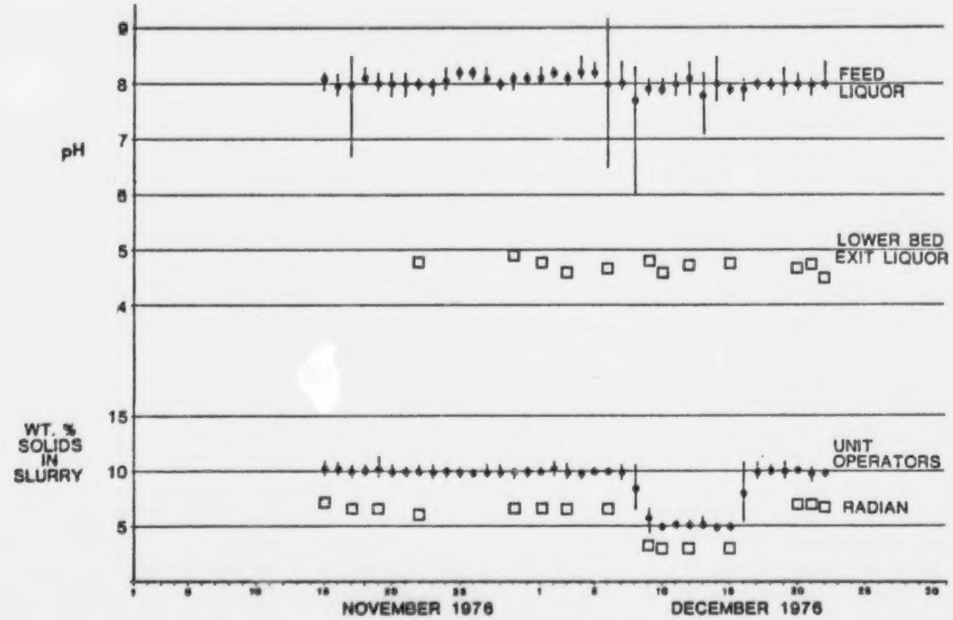


Figure 5-1. Scrubber removal data for Phase I.



Figures 5-2. Slurry properties - Phase I.

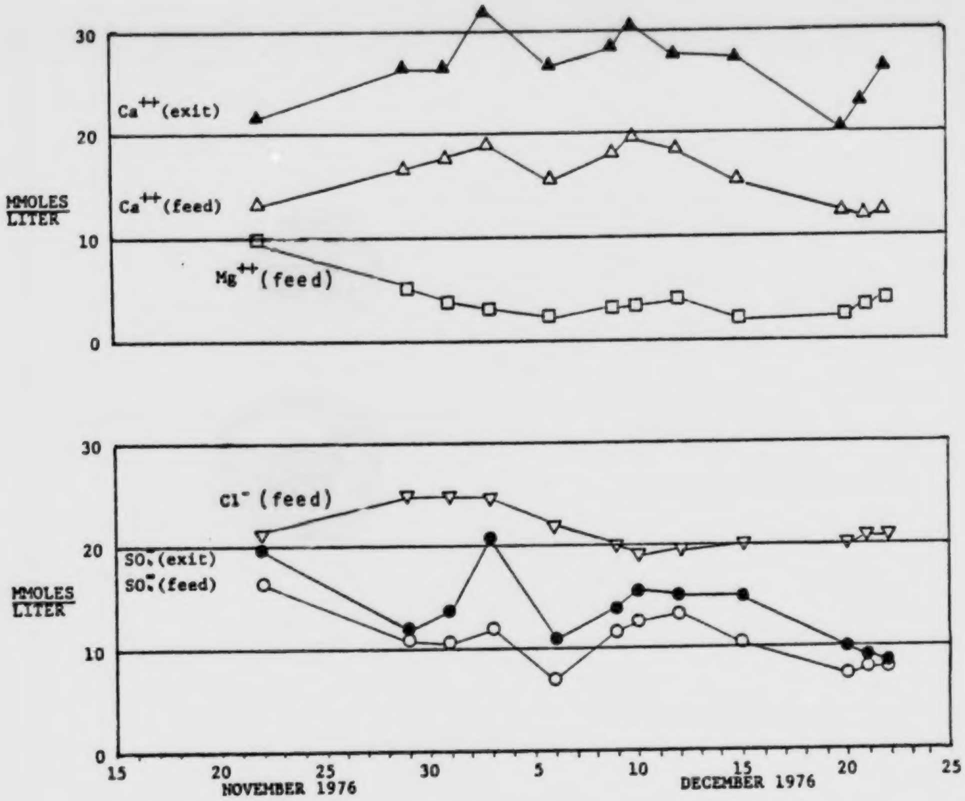


Figure 5-3. Liquid phase concentrations - Phase I.

The calcium solids dissolution which occurred in the Paddy's Run system at base case conditions is a significant operating characteristic. Roughly 1/3 to 1/2 of the total alkalinity required for SO_2 removal was being derived from calcium sulfite dissolution in the scrubber. A significant portion of the sulfate ion increase was also due to solids dissolution since some sulfate exists in a solid solution with the calcium sulfite. The large amount of solid phase alkalinity required was due to the relatively low L/G employed which limited the total available liquid phase alkalinity. The low slurry residence time on the marble beds (20-30 seconds) provided the time required for the relatively slow solid dissolution reactions to occur. Thus, the mechanical design of the Paddy's Run marble bed scrubbers resulted in the large percentage increase in calcium ion concentration across the scrubber.

If the concentrations of both Ca^{++} and $SO_4^=$ increase across the scrubber, the gypsum relative saturation will also increase. This effect is shown in Figure 5-4. Since the system oxidation level remained below 15 percent during Phase I, the scrubber feed liquor remained subsaturated with respect to gypsum due to the coprecipitation mechanism. The lower bed downcomer liquor was also subsaturated during most of this test phase except for a short period when the system oxidation level approached 15 percent and the inlet relative saturation approached 1.0. The increased gypsum relative saturation across the scrubber, which was caused primarily by calcium solids dissolution, did not create scaling problems during Phase I because the oxidation rate remained low.

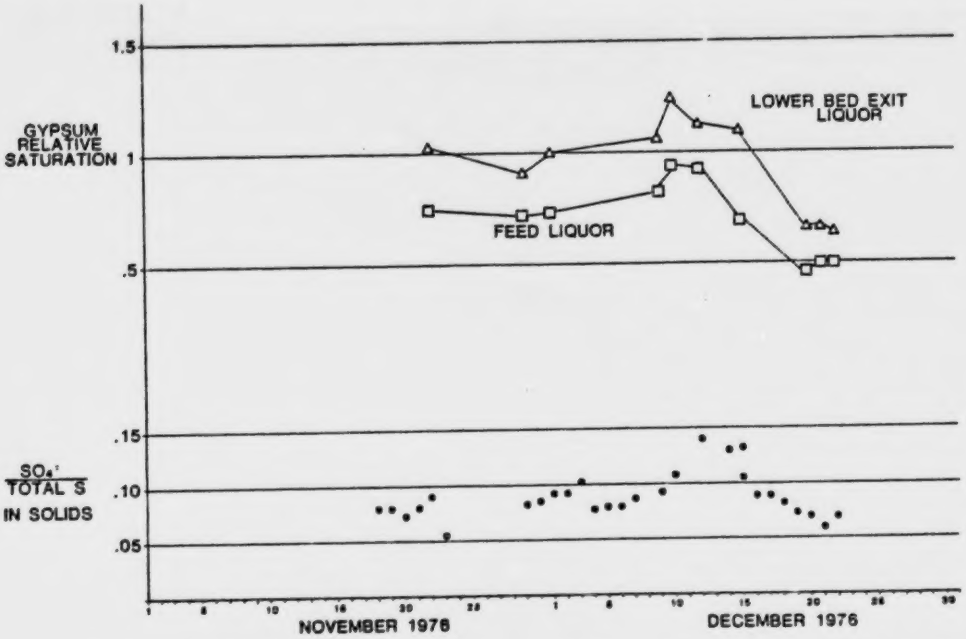


Figure 5-4. Relative saturation and percent oxidation - Phase I.

The effects of a scrubber liquid feed rate change are shown in Table 5-1. Although the oxidation levels and therefore the gypsum relative saturation values were higher than for base case conditions during both of these L/G tests, operation at the higher L/G showed an increased removal efficiency and a lower relative saturation increase than did operation at a lower L/G.

TABLE 5-1. L/G VARIATION TEST RESULTS

	Phase I base case L/G=7.5 ℓ/Nm^3	Data from 12/3/76 Reduced L (-33%) L/G=5	Increased L (+33%) L/G=10
SO_2 Removal	75-80	64	81
Outlet liquor pH (lower bed)	4.8	4.6	5.2
Gypsum relative saturations:			
Scrubber feed liquor	0.7-0.75	.89	0.83
Lower bed effluent	0.9-1.0	1.54	1.24

Phase II - Commercial Lime Testing

Phase II was started with commercial lime additive on March 10, 1977. However, the scrubbing liquor was found to be contaminated with carbide lime process water during the early portion of the test period. As a result, meaningful test data could not be acquired until early April.

In some respects, operation with commercial lime was very similar to operation with carbide lime. As shown in Figure 5-5, the SO_2 removal obtained with commercial lime at base case conditions was equivalent to that obtained in Phase I. Dissolution of calcium solids in the scrubber was still necessary to provide the alkalinity needed for SO_2 removal. Figure 5-6 shows that the percentage increases in Ca^{++} (60-70 percent) and $SO_4^{=}$ (20-30 percent) were equivalent to the increases noted across the scrubber during Phase I.

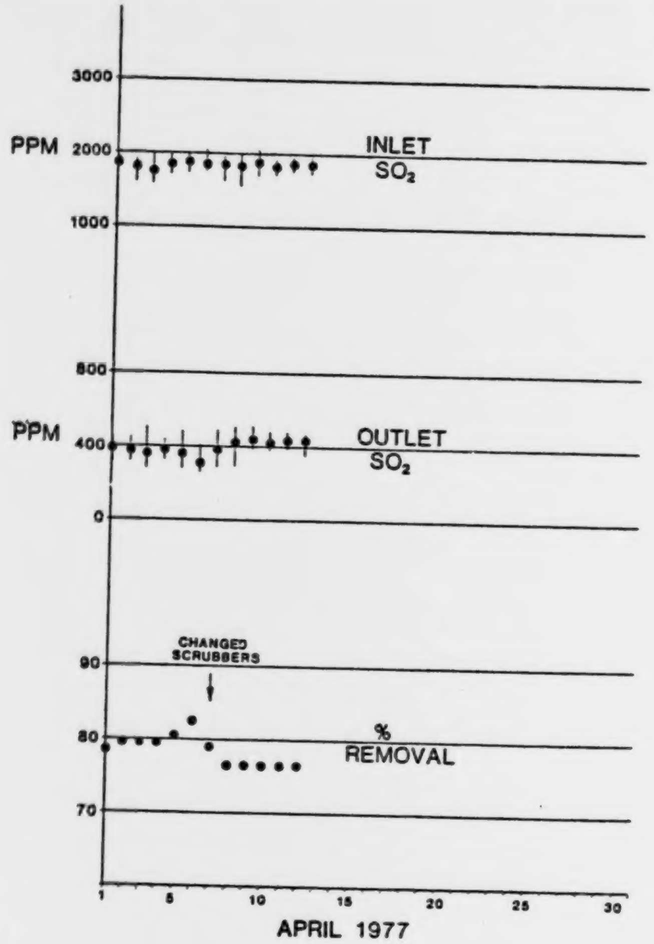


Figure 5-5. Scrubber removal data for Phase II.

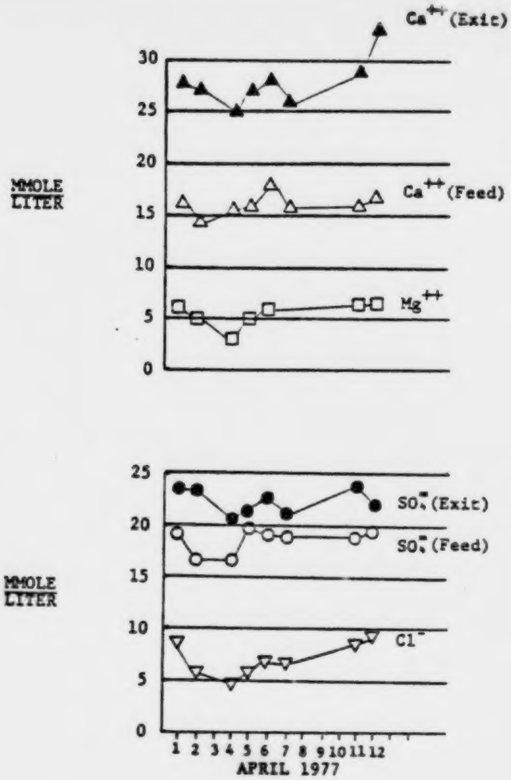


Figure 5-6. Liquid phase concentrations - Phase II.

The major difference between operation with commercial lime and carbide lime was that the oxidation rate was higher with commercial lime. The effect of this change in oxidation rate is shown in Figure 5-7.

In the case of carbide lime operation, the relative saturation of gypsum in the scrubber feed stream remained about 0.7 to 0.75 at an oxidation fraction of 0.1. Due primarily to the dissolution of calcium solids, the gypsum relative saturation of the lower bed exit stream increased about 30 percent to between 0.9 to 1.0.

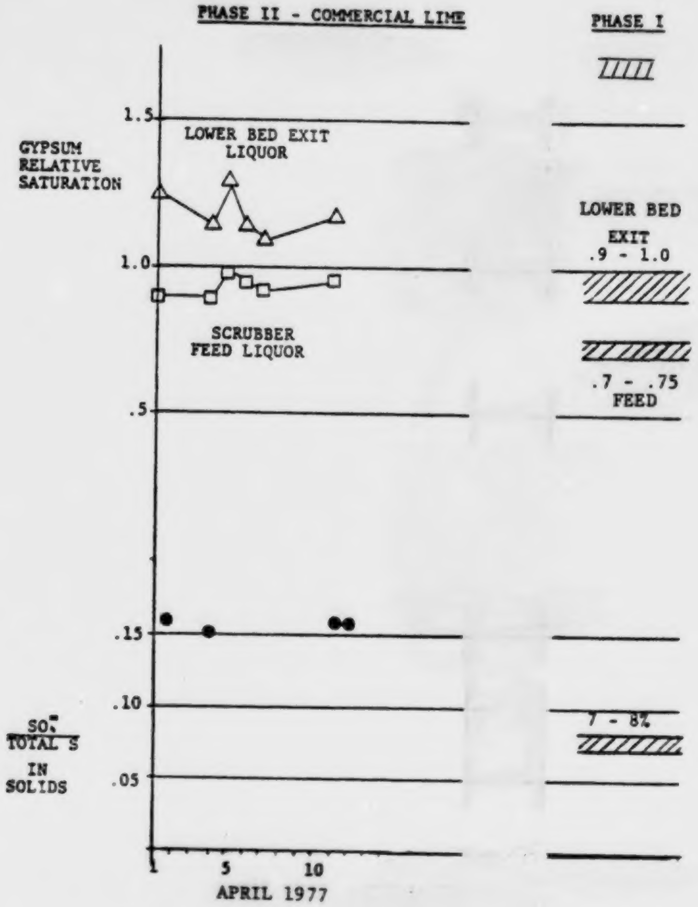


Figure 5-7. Comparison of oxidation rate and gypsum relative saturation values - Phase I vs. Phase II.

Operation with commercial lime resulted in a sulfite oxidation fraction of 0.15. As a result, the scrubber feed gypsum relative saturation varied between 0.9 to 1.0. Since the increases in Ca^{++} and $SO_4^=$ across the lower bed were approximately equal during the two phases, the increase in gypsum relative saturation was about 30 percent in both Phase I and Phase II. The resulting lower bed effluent gypsum relative saturation was between 1.1 and 1.3 during Phase II.

Gypsum relative saturations less than 1.3 are below what is generally considered to be the critical scaling limit (2). However, the lower bed effluent stream is a composite of the liquor leaving the entire lower bed. Regions on the bed which were burdened with higher than average SO_2 loadings would have experienced higher than average gypsum relative saturations. In this situation, localized scaling might be expected. This is exactly what was observed throughout Phase II, even when the scrubber liquid rate was raised to its maximum value.

The results from Phases I and II support the data gathered during coprecipitation laboratory studies which were performed by Radian for EPA (1). In both phases, the gypsum relative saturation of the scrubber feed liquor approached one as the solid sulfate/ total sulfur ratio approached 0.16. This is about the maximum amount of sulfate which can be incorporated into the calcium sulfite hemihydrate crystal lattice. Infrared scans run on solid samples from both phases indicate that all of the sulfate in the solid phase present was calcium sulfite-sulfate solid solution. If any of the gypsum solids formed in the scrubber during Phase II were carried to the reaction tank, they were redissolved because the reaction tank liquor was subsaturated with respect to gypsum.

Additionally, further work sponsored by the EPA has identified several reduced sulfur compounds as well as polynuclear aromatics in the carbide lime (3). Thiosulfate is one of these compounds, which is a known inhibitor of the oxidation reaction of sulfite to sulfate. It is very likely that the successful operation of the Paddy's Run system with carbide lime is a result of these contaminants minimizing the sulfite oxidation rate. When commercial lime was used without the inhibitors present, the sulfate formation rate was greater than what could be removed by the coprecipitation mechanism. This subsequently resulted in scale formation in the scrubber.

Phase III - Magnesium Addition Testing

Once it was recognized that scaling was unavoidable with commercial lime at base case conditions, several options were considered:

- Increasing the scrubber L/G to lower the pickup of SO_2 (and $SO_4^=$) per unit volume of slurry. This would also be beneficial from the standpoint of lowering the requirement for calcium solids dissolution in the scrubber. An L/G increase could be accomplished by either

    - increasing the slurry flow rate (L)
    - Decreasing the gas flow (G)

    A liquid rate increase in the LG&E system was probably the most desirable option, but this would have involved considerable time and expense due to the mechanical changes required. A significant gas flow decrease was not feasible because a minimum gas rate was required to hydraulically maintain liquid levels on the marble beds.

- Growing larger solids to decrease the solids dissolution rate in the scrubber (this would effectively accomplish the same thing as an L/G increase except that it would lower the removal). Unfortunately, the extent of the operator's ability to control this factor was not known since the tests which would establish this were not to be executed until Phase IV.

- Adding magnesium to increase the soluble liquid phase alkalinity (which would also decrease the requirement for solids dissolution).

Basically, the third option was selected because of the problems and/or the uncertainties associated with the first two options. The results achieved by adding $Mg(OH)_2$ to the hold tank in slurry form are shown in Table 5-2 and Figure 5-8.

TABLE 5-2. IMPACT OF MAGNESIUM ADDITION ON SCRUBBER PERFORMANCE

	Commercial lime Phase II base case conditions	Commercial lime $+Mg(OH)_2$ addition	
	Mg <10 mmole/ℓ (<200 ppm)	Mg = ∼90 mmole/ℓ (∼2000 ppm)	Mg = ∼ 170 mmole/ℓ (∼4000 ppm)
SO_2 in (ppm)	∼2000	∼2000	∼2000
SO_2 out (ppm)	300-500	50-150	<10
Removal efficiency	∼75%	∼90-95%	99.5^+%

The most dramatic effect of magnesium addition was its impact on the observed SO_2 removal efficiency. As is shown in Table 5-2, magnesium concentrations of 170 mmole/liter (∼4000 ppm) resulted in removal efficiencies above 99 percent. At magnesium concentrations of about 90-95 mmole/liter (∼2000 ppm) removals between 90 and 95 percent were obtained which was still significantly higher than the 75 percent achieved with either commercial or carbide lime alone.

0.05 and the gypsum relative saturation was below 0.2 throughout the scrubbing loop. However, when the magnesium concentration was dropped to 90 mmole/liter (∿2000 ppm), the scrubber effluent pH's dropped, and calcium dissolution was noted in the scrubber. During the same period, the solid phase sulfate/total sulfur ratio rose to 0.13, and gypsum scaling was observed on scrubber internals. The gypsum scale thus formed was dissolved as the magnesium level was again increased.

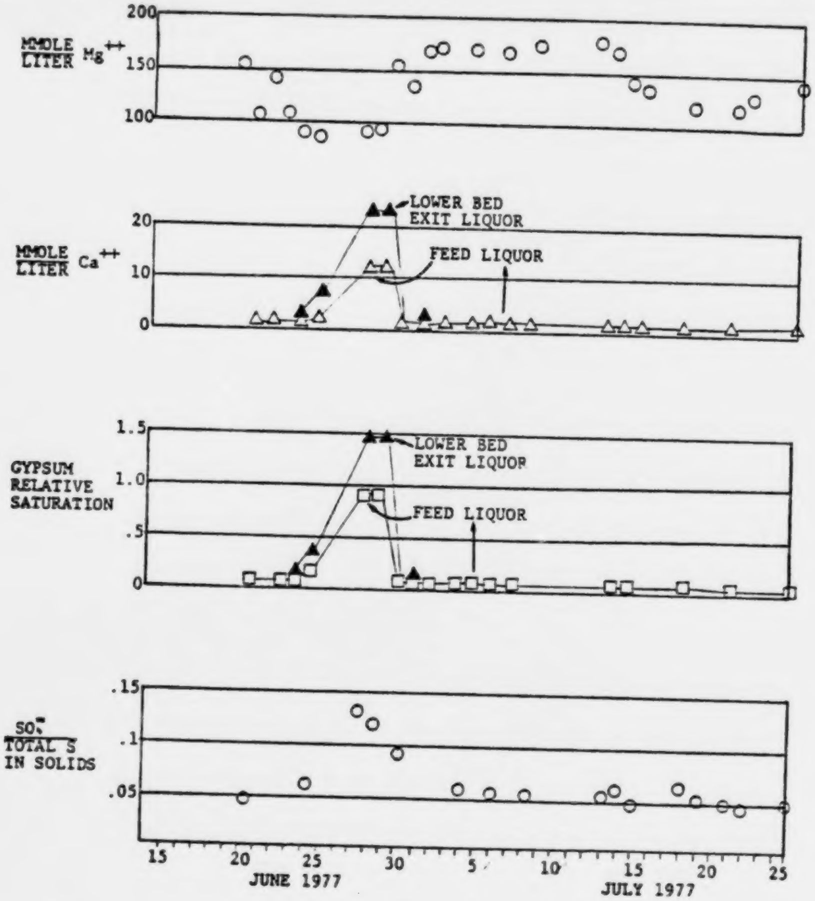


Figure 5-8. Impact of magnesium level on oxidation and gypsum scaling potential.

Operation with magnesium during Phase III established operable conditions in the Paddy's Run system using commercial line. The benefits were twofold. First, the increased liquid phase alkalinity eliminated the need for calcium sulfite dissolution on the marble beds and eliminated the scaling conditions observed in Phase II. Second, the increase in magnesium also reduced the fraction of the sorbed SO_2 which was oxidized to sulfate. (Although there were significant amounts of soluble sulfate leaving the system with the liquor, the overall oxidation fraction was still considerably less in Phase III than in Phase II.) Together, these effects resulted in very efficient scrubber system operation.

It was noted, however, that operation with magnesium addition is not without its drawbacks. It appears that high magnesium levels can lead to waste solids settling and dewatering problems. During Phase III, operation with magnesium concentrations above 180 mmole/liter led to clarifier operating problems. It seems that the increased magnesium levels increased the soluble sulfite and sulfate levels and created conditions which were conducive to excessive nucleation. This created small, somewhat amorphous solid crystals which would not settle very efficiently. Clarifier settling problems were observed between July 12 and July 19, 1977. A reduction in the magnesium level reestablished the formation of rosette crystal structures which settled much more quicker.

Phase IV - Reaction Tank Modifications

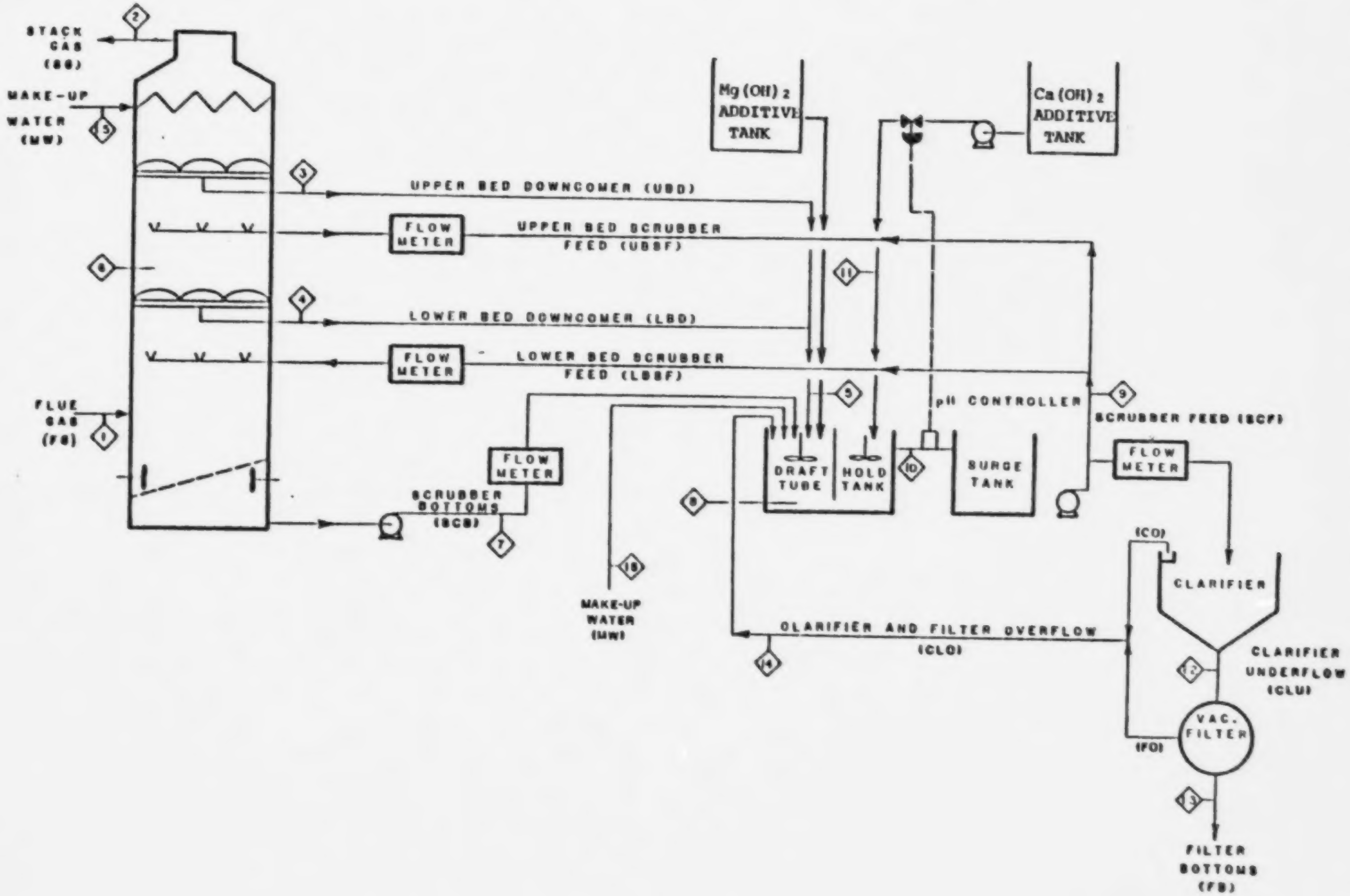
Two reaction tank modifications were tested during Phase IV operation. First, the draft tube effect was eliminated by relocating the lime additive point from the draft tube to the main reaction tank (Figure 5-9). In a second test, the residence time of the reaction tank system was reduced from about 35 minutes to about 5 minutes by bypassing the main reaction tank (Figure 5-10). Both tests were conducted with $Mg(OH)_2$ addition.

Operation in both configurations proved to be successful. As expected, the effects of magnesium on SO_2 removal for each configuration were quite similar to those shown in Phase III. However, there were some differences in the gypsum relative saturations and the solid phase sulfate/total sulfur ratios for the two configurations. These differences are shown in Figure 5-11. It can be seen that the oxidation was somewhat higher during operation in the reduced residence time configuration.

Draft Tube Elimination Test

Basically, the effects of magnesium on total system operation in this configuration were similar to those experienced in Phase III. With the lime additive point change, the system remained operable at magnesium levels above 100 mmole/liter. Conditions which were subsaturated with respect to gypsum were present throughout the system, and the solid phase sulfate/total sulfur ratio remained about 0.05 to 0.07. When the magnesium level was reduced and maintained below 100 mmole/liter however, significant calcium dissolution occurred in the scrubber, and the oxidation fraction and gypsum relative saturations approached inoperable levels.

The main effect expected from the lime additive point change was an alteration in the product crystal structure. When the lime additive enters the draft tube, lime particles dissolve directly into the scrubber effluent liquor, which is relatively high in soluble sulfite and has a low pH. Locally high relative


STACK GAS (SG)
MAKE-UP WATER (MW)
FLUE GAS (FG)
UPPER BED DOWNCOMER (UBD)
FLOW METER
UPPER BED SCRUBBER FEED (UBSF)
LOWER BED DOWNCOMER (LBD)
FLOW METER
LOWER BED SCRUBBER FEED (LBSF)
FLOW METER
SCRUBBER BOTTOMS (SCB)
Mg(OH)2 ADDITIVE TANK
Ca(OH)2 ADDITIVE TANK
pH CONTROLLER
DRAFT TUBE
HOLD TANK
SURGE TANK
SCRUBBER FEED (SCF)
FLOW METER
MAKE-UP WATER (MW)
CLARIFIER AND FILTER OVERFLOW (CLO)
(CO)
CLARIFIER
CLARIFIER UNDERFLOW (CLU)
VAC. FILTER
(FO)
FILTER BOTTOMS (FB)
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18

Figure 5-9. Hold tank modification - draft tube elimination.

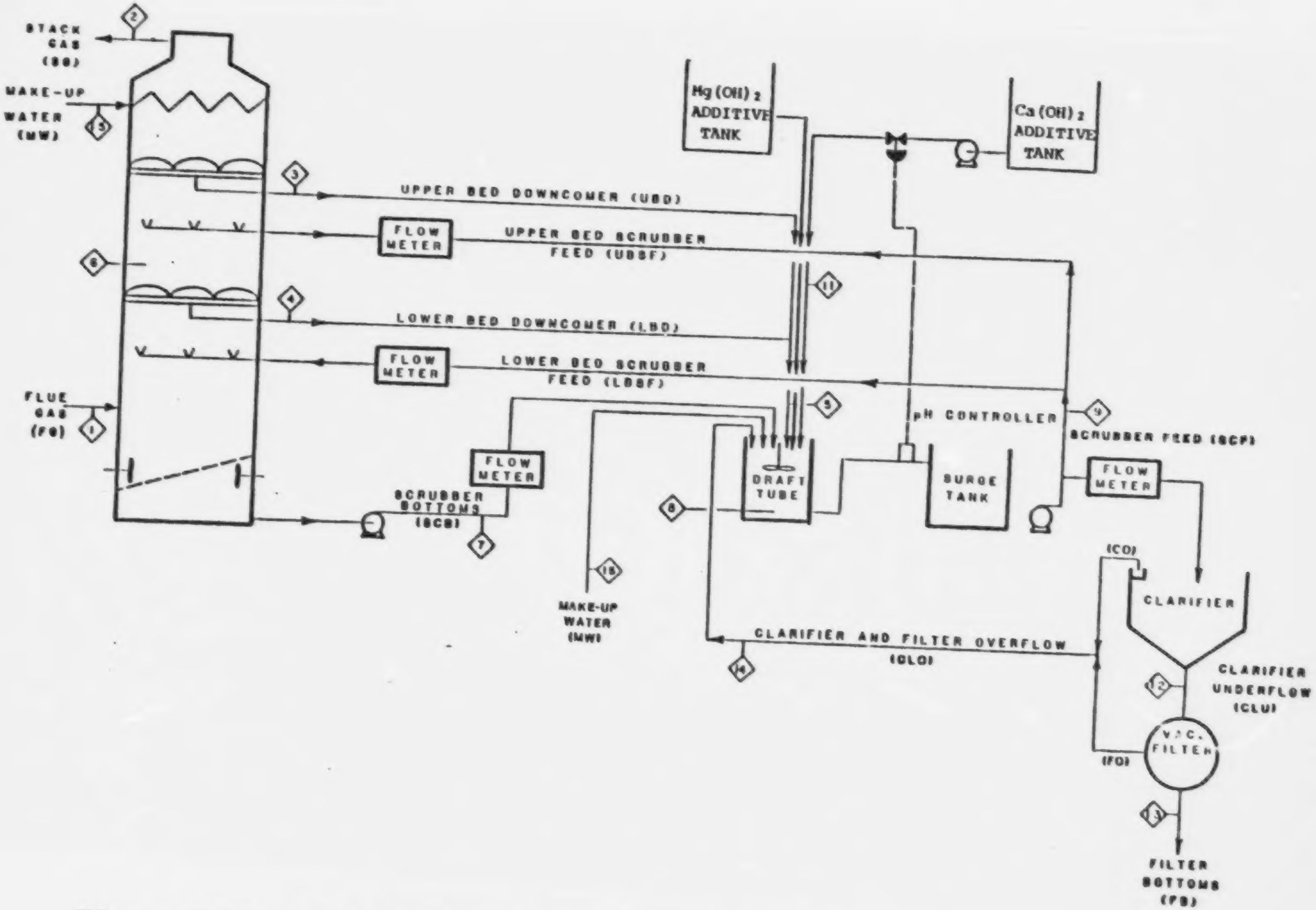
STACK GAS (SG)
2
MAKE-UP WATER (MW)
15
3
UPPER BED DOWNCOMER (UBD)
FLOW METER
UPPER BED SCRUBBER FEED (UBSF)
6
4
LOWER BED DOWNCOMER (LBD)
FLOW METER
LOWER BED SCRUBBER FEED (LBSF)
FLUE GAS (FG)
1
Mg(OH)2 ADDITIVE TANK
Ca(OH)2 ADDITIVE TANK
11
5
pH CONTROLLER
9
SCRUBBER FEED (SCF)
FLOW METER
SCRUBBER BOTTOMS (SCB)
7
DRAFT TUBE
8
SURGE TANK
FLOW METER
16
MAKE-UP WATER (MW)
(CO)
CLARIFIER
CLARIFIER AND FILTER OVERFLOW (CLO)
14
CLARIFIER UNDERFLOW (CLU)
12
VAC. FILTER
(FO)
13
FILTER BOTTOMS (FB)

Figure 5-10. Hold tank modification - five minute residence time.

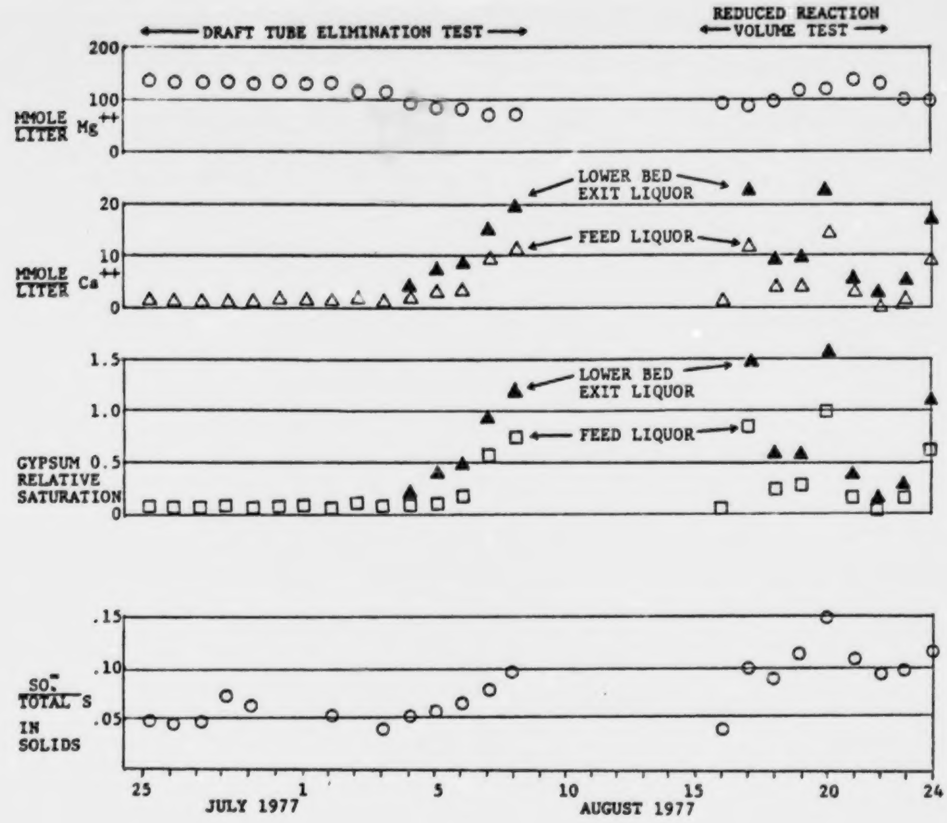

Figure 5-11. Impact of Mg on system operation during Phase IV.

saturations thus occur in the region of the dissolving solid $Ca(OH)_2$ particles. These high relative saturations promote nucleation. In the configuration where lime enters the main reaction tank liquor which has a higher pH and lower soluble sulfite concentration. Since the localized relative saturations generated in this situation would not be expected to be as high, more orderly crystal growth should be promoted by the "no draft tube" configuration.

The results from the draft tube elimination test support this theory. The lime additive point was moved from the draft tube on July 25, 1977. Almost immediately, the crystal morphology began changing from the rosettes which were produced during Phase III to structures which were more platelet-like. During this transition, solids settling problems were encountered. However, continued operation in the no draft tube configuration and a reduction in magnesium concentration resulted in calcium sulfite platelets similar to those produced in many limestone FGD systems. The large platelets formed during the latter portion of this test settled well and clarifier and filter efficiencies were restored.

Reduced Reaction Tank Volume

The objective of the reduced reaction volume test was to assess system operability with the main reaction tank eliminated from the scrubbing loop. The system did remain operable in this configuration although some operating differences are apparent in Figure 5-11.

The main difference between operation with the reduced residence time tank in Phase IV and operation with the larger tank in Phase III was the oxidation rate. For equivalent magnesium concentrations, the solid phase sulfate/total sulfur ratio was higher during the reduced reaction volume testing. In fact, at a magnesium concentration of about 120 mmole/liter, the solid phase oxidation fraction in the reduced volume testing (.12) was roughly double that seen during Phase III (0.06).

This result is contrary to what might be expected. If the oxidation rate in the hold tank were significant, a reduction in total volume (and total air-liquid surface area) should result in lower oxidation rates. If the major portion of the oxidation normally occurs in the scrubber, then the reduction in residence time would be expected to have little effect.

One operating variable which may have had a major effect on the oxidation rate during this period was the liquid level in the reaction tank. Since the volume of liquor in the system had been reduced by almost an order of magnitude, liquid level control was more sensitive during the reduced residence time test period. As a result, the liquid level in the draft tube and surge tank fluctuated more than during normal operation. The top agitator blade in the draft tube was often close to the liquid surface. At times, the exposed agitator created a frothing effect. The disturbance of the air-liquid interface may have increased the O_2 transfer from the air to the scrubbing liquor which could account for the increased oxidation rate. Thus, fluctuations in liquid levels may explain the increased oxidation seen in the reduced volume testing. Unfortunately, sufficient time for sealing the draft tube and checking this hypothesis was not available.

Other than the variance in oxidation, the results observed during the reduced residence volume tests were anticipated. Since testing in Phase III indicated that most of the solid-liquid reactions were tanking place in the draft tube, few changes were expected as a result of eliminating the main reaction tank. Due to the reduced residence time, a slight increase in the reaction tank liquor's calcium sulfite relative saturation was noted. The crystals which resulted from operation in the reduced residence time configuration were rosettes which were similar to those noted in Phase III. Since surface nucleation in the draft tube was a predominant precipitation mechanism for both reaction tank configurations, this result would be expected.

Phase V - Chloride Addition Testing

The final test phase was devoted to determining the effect of increased chloride levels on system chemistry. $CaCl_2$ was added to the system to increase the chloride level from 10 mmole/liter to 80 mmole/liter. Since operating time was limited during this phase, the magnesium level was increased simultaneously to keep the system operable. One mole of magnesium added for each two moles of chloride was found to maintain the scrubbing solution's liquid phase alkalinity. The results of Phase V testing are shown in Figure 5-12.

Since the magnesium concentration was increased in conjunction with the increase in chloride, extensive data concerning the independent effect of chloride is not available. However, data gathered early in this phase before the system was at steady state gives an indication of the chloride effect. An initial spike in chloride concentration of 270 mmole/liter occurred on August 24. The results of operating at this high chloride concentration were as expected. The calcium concentrations were

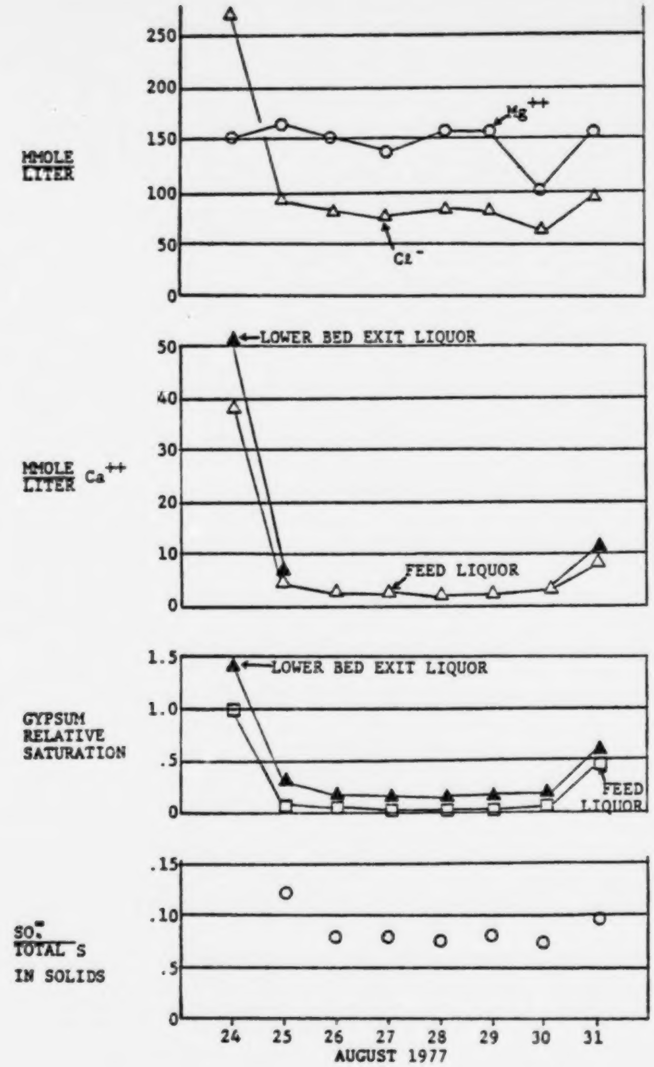

Figure 5-12. Phase V system chemistry parameters.

higher than normal; an initial spike was noted in the oxidation rate; significant dissolution of solid phase calcium in the scrubber was evident; and scaling conditions were observed on the lower bed. As the chloride concentration in scrubbing slurry and the clarifier liquor equalized at about 80 mmole/liter, the solid phase oxidation fraction dropped to below 0.1 and subsaturated conditions were again measured in lower bed effluent liquor. The need for calcium solids dissolution was eliminated as the magnesium/chloride ratio increased.

The main effect of chloride during Phase V can be explained by considering the impact of chloride on the liquid phase alkalinity. Chloride is a soluble species in lime/limestone systems. As the chloride ion concentration increases, the concentrations of available cations (usually magnesium, calcium, or sodium) must also increase to maintain an electrically neutral solution. In the absence of sufficient magnesium and sodium, the calcium ion concentration will increase as chloride increases. Since calcium salts such as sulfite, sulfate, and carbonate are relatively insoluble, as the calcium concentration increases, the concentration of alkaline anions such as sulfite and carbonate must decrease to satisfy solubility constraints. There, the effect of increasing the chloride is to displace less soluble, more alkaline species from solution. These effects of high chloride concentrations on system operation are clearly indicated in Figure 5-12.

As mentioned previously, the magnesium concentration was increased to offset the addition of chloride. Since a magnesium level of 125 mmole/liter had maintained system operability at the conclusion of Phase IV and one mole of magnesium electrically balances two moles of chloride, the magnesium concentration was increased to about 160 mmole/liter to offset the 70 mmole/liter increase in chloride. Since the magnesium sulfite and carbonate salts are soluble, the liquid phase alkalinity was essentially the same in Phase V (after the initial spike in chloride) as during Phase IV. The low calcium dissolution rates in the scrubber measured between August 25 and 30 reflect this.

Solid Solution Chemistry

One of the major objectives of this program was to determine the basis for the operation of the Paddy's Run system in a mode which was subsaturated with respect to gypsum. During the course of this program, the solid phase sulfate/total sulfur ratio was found to have a major impact on the gypsum saturation level in the system's reaction tank liquor. This same result was also found in a laboratory study previously conducted by Radian (1). In Figure 5-13, the field data from the LG&E test program are compared with the correlation of solid phase sulfate/total sulfur versus gypsum relative saturation derived from the laboratory experiments. While there is scatter due to 1) unsteady-state operation, and 2) uncertainties in the gypsum relative saturations and analytical results in Phase I, the results from the field testing show that the reaction tank liquor remained subsaturated when the solid phase sulfate/total sulfur level remained below about 0.16.

It has been hypothesized that changes in variables such as magnesium concentration, chloride concentration, and calcium sulfite precipitation rate would alter the amount of sulfate which could be incorporated into the coprecipitated calcium sulfite-sulfate solids. Such trends were not noted during the field testing, but the effects of changes in these variables could not be separated from the effects of oxidation rate changes. Therefore, the effect of magnesium concentration, chloride concentration, or calcium sulfite precipitation rate on the maximum rate of sulfate incorporation into the calcium sulfite-sulfate solid solution cannot be measured from the data gathered.

It is noted from Figure 5-13 that throughout the majority of the program the reaction tank liquor was subsaturated with respect to gypsum. However, during Phase II and in certain instances during Phases III, IV, and V, increases in the gypsum saturation level in the scrubber led to gypsum scaling. The increases in gypsum saturation were, to a large extent, a result of calcium solids dissolution in the scrubber.

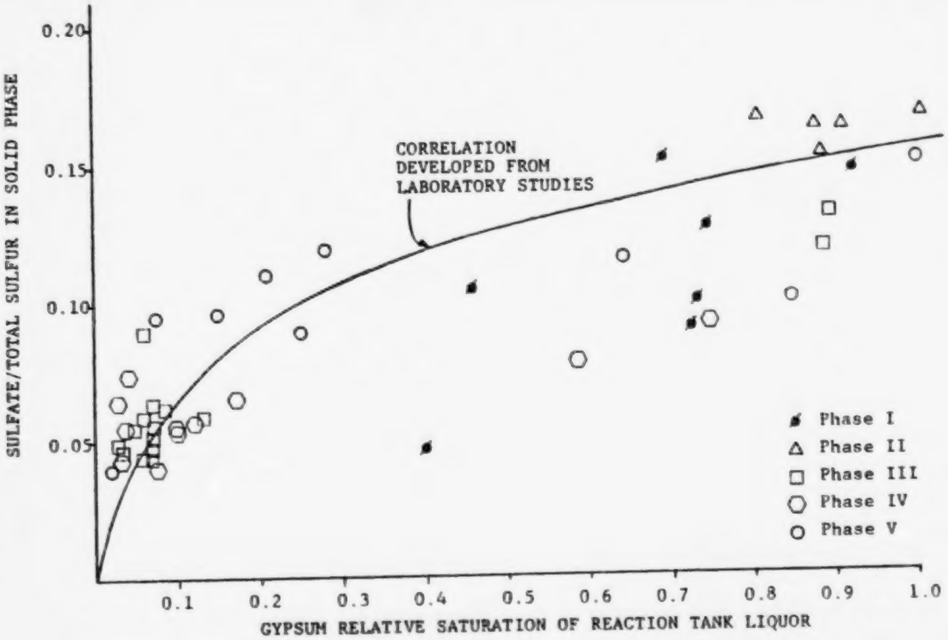

Figure 5-13. Comparison of LG&E field data with laboratory solid solution test results.

APPENDIX A

PHASE I

CARBIDE LIME OPERATION

1.0 SUMMARY

During Phase I of the EPA/LG&E test program the performance of the Paddy's Run system was studied while operating with the system's normal alkaline additive, carbide lime. This was done to provide a comparative basis for subsequent testing with a standard, commercial lime additive.

During the initial portion of Phase I, the system was run at conditions which were typical of normal (previous) Paddy's Run operation. Table 1-1 summarizes these conditions.

During the remainder of Phase I, tests were run to determine the effects of reduced recirculating slurry solids, liquid-to-gas ratio (L/G) changes, and scrubber feed pH changes. The ranges of these variables which were studied during Phase I are also shown in Table 1-1.

TABLE 1-1. SUMMARY OF OPERATING CONDITIONS AT LG&E'S PADDY'S RUN PHASE I TESTING

Parameter	Range	Average
Inlet SO_2 in Flue Gas (ppm)	2130-3120	2600
Outlet SO_2 in Flue Gas (ppm)	278-953	650
Percent SO_2 Removal	66-87	75
Relative Saturation of $CaSO_4 \cdot 2H_2O$ in scrubber feed	0.40-0.95	
Solids Oxidation Fraction	0.035-0.151	
Liquid-to-Gas Ratio (ℓ/Nm^3)		
- Normal conditions	6.9-7.8	
- L/G Tests	5.2-10.4	
Scrubber Feed pH		
- Normal conditions	7.9-8.5	
- pH tests	6.8-9.0	
Weight Percent Solids in Scrubber Feed		
- Normal	6.2-7.1	6.5
- Low solids tests	-	3.0

During the two months of Phase I testing at Paddy's Run, no major operating problems were encountered. Inlet SO_2 concentrations averaged about 2600 ppm, and the removal efficiency averaged 75 percent. The scrubber feed liquor remained subsaturated with respect to gypsum ($CaSO_4 \cdot 2H_2O$). Throughout this test phase the relative saturation of gypsum in the scrubber feed liquor ranged from 0.40 to 0.75. Due to the increases in both liquid phase calcium and sulfate concentrations which occurred across the scrubber, the gypsum relative saturation levels in all three scrubber effluent streams were consistently higher than that of the feed. Generally, the lower bed downcomer liquor (obtained from a stream which closely approximates average scrubber effluent conditions), remained subsaturated with respect to gypsum. Its relative saturation ranged from 0.50 to 1.13. Furthermore, inspection of the marble beds after completion of the Phase I testing showed no evidence of gypsum scale.

The fraction of the SO_2 absorbed which was oxidized during Phase I ranged from 0.035 to 0.151. These values are consistent with the results of laboratory studies which indicate that the Paddy's Run system operates subsaturated because of calcium sulfate coprecipitation with calcium sulfite. At oxidation fractions less than 0.16, all of the sulfate which forms in the liquid phase can coprecipitate and leave the system as a solid solution with the $CaSO_3 \cdot \frac{1}{2}H_2O$. Under these conditions the solution in the reaction tank will remain subsaturated with respect to gypsum.

The L/G tests produced inconsistent results. One test set showed the expected increase in SO_2 removal as the L/G increased while another test set showed the exact opposite. Fluctuations which were occurring in the inlet SO_2 concentrations during these tests may account for these differences.

No major difference in scrubber performance was seen as the scrubber feed liquor pH was varied between 6.8 and 9.0. SO_2 removal efficiencies remained at approximately 70 percent during this test series.

During the low solids tests the recirculating slurry solids concentration was lowered to three percent by weight. This compares to an average of 6.5 percent during normal operation. The observed removal efficiency was approximately the same as that for normal operation (74 percent). However, the oxidation fraction rose to 0.15. Gypsum relative saturation levels in the scrubber feed were 0.7 to 0.9 for this period. Those in the lower bed downcomer were 1.11 to 1.13. These were the highest steady-state values measured during Phase I.

A unique feature of the Paddy's Run system is the draft tube or mixing well. The scrubber effluent, clarifier overflow, and lime additive streams are premixed in the draft tube before they enter the main reaction tank. The slurry residence time in the draft tube is about 30 seconds when the system is operating at a 35 MW load. Even with this short residence time, rate calculations show that the majority of the lime dissolution and sulfur precipitation which takes place in the reaction tank system actually occurs in the draft tube.

While no major process problems were encountered during Phase I, a significant analytical problem was apparent. Carbide lime contains reduced sulfur species which interfere with Radian's analytical technique for liquid phase sulfite. This type of interference has not been noted with other lime systems. The influence of these interfering species account in part for the low oxidation rates which are observed at Paddy's Run. Thiosulfate has been identified as the major inhibitor of oxidation present in carbide sludge (3). Other compounds which have been identified are primarily polynuclear aromatics. Their low concentrations (ppb) probably reduces any effect they may have on oxidation.

2.0 TEST APPROACH

The initial phase of testing at Paddy's Run involved its normal mode of operation. This included the use of carbide lime as the alkaline additive. Figure 2-1 shows the normal process configuration which was used in this phase.

As part of the characterization task, steady-state operating conditions were established and key process parameters were monitored. Important measurements included gas, liquid, and solid flows; temperatures; pressures; liquid compositions; and system liquid levels. These data were used as a basis for calculating removal rates, sulfite/sulfate precipitation rates, sulfite oxidation rates and lime utilization efficiencies. These results represent "base case" conditions for purposes of comparison with subsequent test results.

Although system operation began in late October, full characterization sample sets were not taken until the end of November. This was due to an unusually high magnesium level in the carbide lime which was supplied by AIRCO. AIRCO used commercial lime in the production of acetylene. The regenerated lime was then sold to LG&E as a scrubber additive.

Five sets of base case samples were taken with the final two being taken after Radian's sulfite analytical technique was altered. Tests 1 and 7 were the base case tests. Tests 2, 3, 8, and 9 were short-term tests designed to measure the effect of scrubber L/G changes. Tests 8 and 9 were L/G tests which were repeated while using the modified sulfite technique. Tests 4 and 5 were used to evaluate low and high scrubber feed pH's. Test 6 was run with a reduced slurry solids content. The specific test conditions for each test are outlined in Section 3.0.

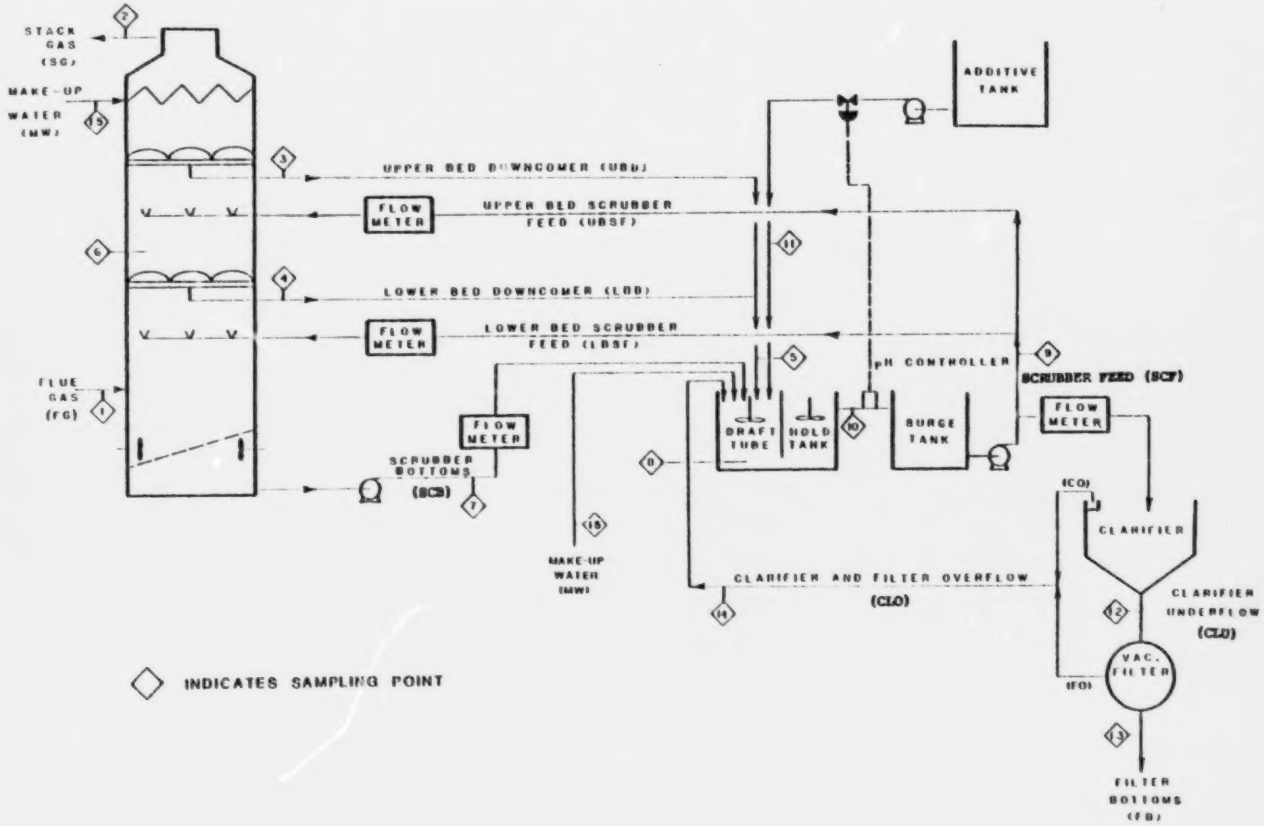
STACK GAS (SG)
MAKE-UP WATER (MW)
FLUE GAS (FG)
UPPER BED DOWNCOMER (UBD)
UPPER BED SCRUBBER FEED (UBSF)
LOWER BED DOWNCOMER (LBD)
LOWER BED SCRUBBER FEED (LBSF)
FLOW METER
SCRUBBER BOTTOMS (SCB)
MAKE-UP WATER (MW)
DRAFT TUBE
HOLD TANK
pH CONTROLLER
SURGE TANK
ADDITIVE TANK
SCRUBBER FEED (SCF)
CLARIFIER
(CO)
CLARIFIER UNDERFLOW (CLU)
VAC. FILTER
(FO)
FILTER BOTTOMS (FB)
CLARIFIER AND FILTER OVERFLOW (CLO)
INDICATES SAMPLING POINT
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Figure 2-1. Carbide lime testing configuration.

3.0 PHASE I RESULTS

The process and analytical data gathered during the Phase I testing are presented in this section. Figure 3-1 summarizes the important Phase I data. The detailed process results are presented in Section 3.1, and the analytical results are presented in Section 3.2.

3.1 Process Data

Figure 3-1 shows that, except for a few inspection periods and an AIRCO (LG&E lime supplier) operating problem, scrubber operation was continuous during Phase I. The process measurements gathered during Phase I testing are presented in Table 3-1.

As indicated by the manual gas phase SO_2 determinations shown in Table 3-1, the SO_2 removal efficiency generally remained between 70 and 80 percent during Phase I. In the early part of November, higher efficiencies were noted, but these decreased as the high magnesium level was lowered in the system. In Phase I, the inlet gas SO_2 measurements ranged between 2100 and 3100 ppm while the outlet concentrations varied from 280 to 930 ppm. Although the DuPont readings were lower than the manual determinations listed above, the results from the DuPont measurements were sufficiently consistent to indicate operating trends.

No major changes in pH were encountered in the scrubber feed other than those during the pH sensitivity tests conducted on December 6. Normally, the solids concentration averaged 6.5 weight percent in the scrubbing slurry. The low solids test (Test 6) was run at three percent solids. Referring to Figure 3-1, it is seen that the weight percent solids values determined

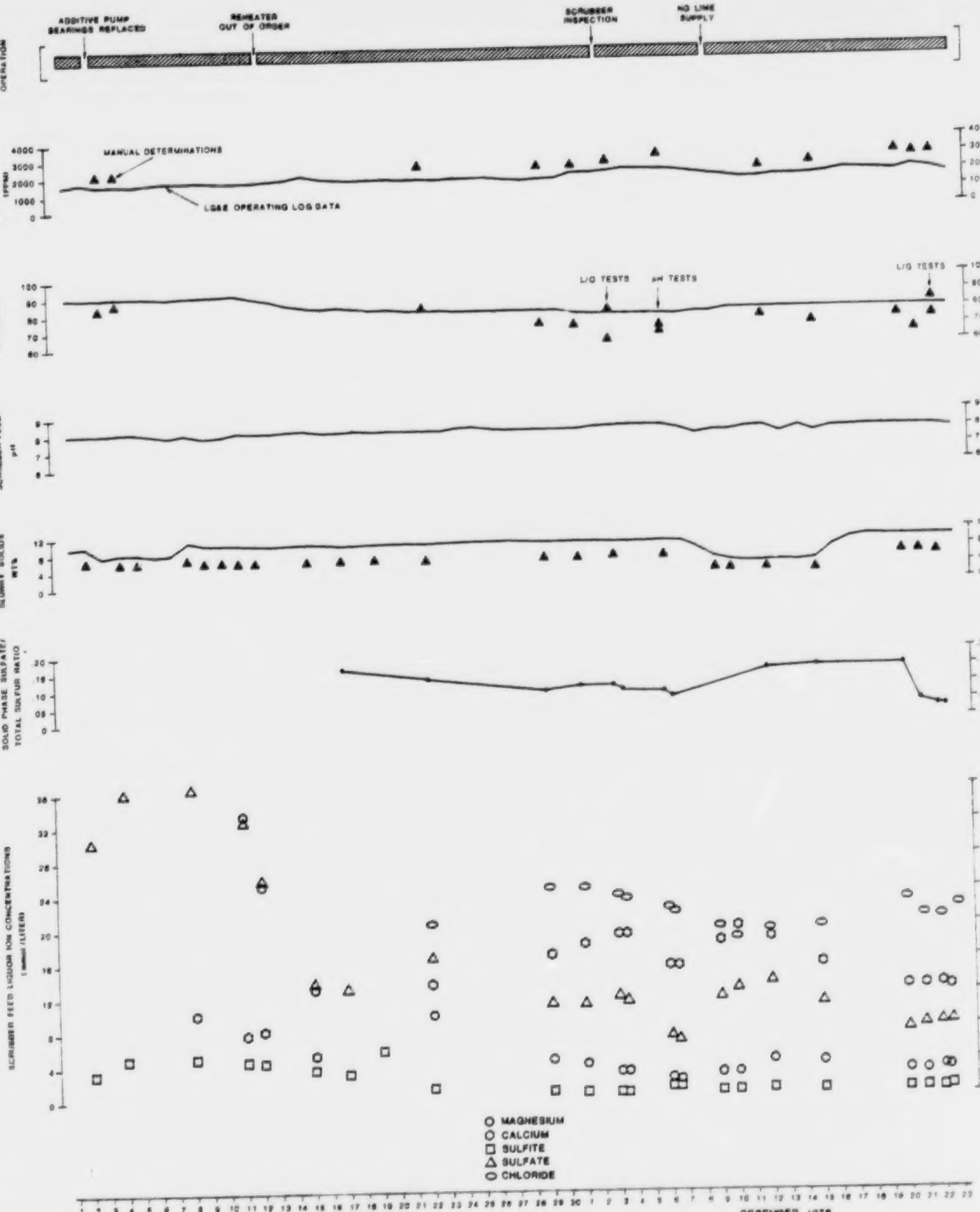


Figure 3-1. Operating data summary for Phase I carbide lime testing.

TABLE 3-1. PHASE I - PROCESS MEASUREMENTS

	Carbide Lime Base Case			L/G Tests		pH Tests		Low solids test		Repeat base case		L/G tests	
	Test #1 Nov. 22	Test #1 Nov. 29	Test #1 Dec. 1	Test #2 Dec. 3	Test #3 Dec. 3	Test #4 Dec. 6	Test #5 Dec. 6	Test #6 Dec. 12	Test #6 Dec. 15	Test #7 Dec. 20	Test #7 Dec. 21	Test #8 Dec. 22	Test #9 Dec. 22
Flue Gas (Nm^3/hr dry)	186,000	175,000	188,000	175,000	175,000	174,000	174,000	172,000	183,000	178,000	178,000	175,000	174,000
SO_2 inlet (ppm)	2,470	2,560	2,370	2,600	2,730	2,940	2,690	2,130	2,480	3,034	2,710	2,650	3,120
SO_2 outlet (ppm)	470	665	646	941	516	953	812	510	718	784	930	426	809
Removal efficiency (%)	81	74	73	64	81	68	70	76	71	74	66	84	74
Scrubber feed (ℓpm)	22,700	→	→	15,100	30,300	20,700	22,500	22,700	→	→	→	15,300	27,400
Upper bed	11,400	→	→	7,570	15,200	11,400	11,200	11,400	→	→	→	7,760	13,600
Lower bed	11,300	→	→	7,570	15,100	11,300	→	→	→	→	→	7,540	13,800
L/G (ℓ/Nm^3)	7.3	7.8	7.2	5.2	10.4	7.8	7.8	7.8	7.4	7.6	7.6	5.2	9.5
Scrubber feed pH	8.3	8.5	8.4	8.1	8.4	6.8	9.0	8.0	8.4	7.9	8.2	8.0	8.0
% Slurry solids	6.2	6.7	6.6	-	6.6	6.6	6.6	3.0	3.0	6.9	7.0	6.7	6.7
Scrubber bottoms (ℓpm)	3,400	3,400	3,390	3,270	3,390	3,510	3,410	3,390	3,410	3,410	3,860	3,630	3,410
Clarifier feed (ℓpm)	680	492	484	394	690	606	560	-	-	712	681	416	712
Clarifier overflow (ℓpm)	340	-	-	340	-	-	-	-	-	-	-	-	-
Filter bottoms (kg/min)	-	94	-	95	95	-	-	-	-	-	-	-	-
Lime additive (ℓpm)	115	105	106	85	123	110	141	139	115	128	103	87	128
Makeup water (ℓpm)	-	106	-	-	-	-	-	-	-	-	-	-	-

Notes: System reaction volume - 860,000 liters
Reject rate from each bed is equal to the scrubber bottoms flow. Lower bed/Upper bed ratio is ~/.5.
Approximately 190 liters/min evaporate from lower bed.

by LG&E operators were consistently higher than manual determinations. However, these numbers were used on a qualitative basis as a means of monitoring the system.

The oxidation fraction as determined from an analysis of the solids ranged from 0.035 to 0.15 during Phase I. The highest oxidation rates were recorded during the low solids tests.

A very thin build-up of gypsum scale on the chevron mist eliminator blades was noted after Phase I. The rate of build-up posed no operating problem. The scaling was probably due to the relatively low SO_2 removal efficiency of the scrubber and to an intermittent wash system.

3.2 Analytical Data

Table 3-2 presents the liquid and solid phase analyses for all Phase I samples. Also included in Table 3-1 are computer calculated relative saturations and SO_2 equilibrium partial pressures. Gypsum relative saturations generally remained below 1.0 and visual inspections revealed only a slight scale on the mist eliminators at the end of Phase I. Certain tests produced near scaling conditions, such as the low L/G and low solids tests. No operational problems resulted from these conditions, however.

As a result of the sulfite analytical problems which were experienced during Phase I, experiments were conducted on-site to 1) document the existence of an interference in the sulfite analytical technique, and 2) supply information concerning the nature of the interference such that possible solutions to the problem could be found. Most of this work occurred during the low solids test period (Test 6).

TABLE 3-2. CHEMICAL DATA SUMMARY

Sample identification				Slurry properties			Liquid analyses (mmol/liter)							Solid analyses (mmol/g)						Computer results		
Test	Date	Stream[1]	Time	pH	Temp (°C)	% Solids	Ca^{++}	Mg^{++}	Na^{+}	Cl^{-}	CO$_3^{=}$	SO$_3^{=}$	SO$_4^{=}$	Ca^{++}	Mg^{++}	CO$_3^{=}$	S.SO$_4^{=2}$	T.S.	Ox Frac	CaSO$_3$RS	CaSO$_4$RS	P*SO$_2$(PPM)
Line out	11-2	SCF	10:30	-	-	6.6						3.2	30.3									
	11-4	SCF	9:15	-	-	6.2						-	-									
		UBD	15:00	6.0	43	-						14.5	36.7									
		LBD	15:10	5.7	45	-						15.1	40.0									
		SCE	15:30	8.6	46	6.5						4.7	36.7									
	11-5	SCF	8:30	-	-	6.4																
		SCF	13:45	-	-	6.4																
		LA	14:00	-	-	24.4																
	11-8	SCF	9:30	8.3	47	7.1	~10.0					5.16	40.0									
	11-9	SCF	9:00	-	-	6.3																
		SCF	15:00	-	-	6.1												7.0				
		LBD	15:10	-	-	-	15.7															
	11-10	SCF	9:15	-	-	6.4																
		MW	11:00	-	-	-																
		LA	11:00	-	-	-																
	11-11	SCF	9:00	-	-	6.3	7.52	33.3	-	-	-	4.58	32.4				.67					
	11-12	SCF	10:30	8.0	44	6.6	8.08	25.0	-	-	-	4.34	25.6			.65	.67					
	11-15	SCF	9:15	8.5	46	7.2	5.12	12.7	-	-	-	3.5	13.3									
		LA	9:15	-	-	22.4																
		LA	16:00	-	-	-																
	11-17	SCF	10:15	-	-	6.6																
		SCF	14:00	8.5	45	-						3.05	12.6				1.02	6.53	.156			
	11-19	SCF	9:30	8.3	45	6.7						5.4				.89						
1[3]	11-22	SCF	13:30	8.3	46	6.2	13.4	9.7	2.7	20.4	.6	1.02	16.2	7.24	.16	-	.82	6.48	.127	3.04	.74	.000006
		LBD	11:50	4.8	45		21.7	10.5	3.4	21.1	2.1	17.2	19.7									
		UBD	11:30	5.1	45		18.9	9.9	2.8	20.8	2.0	14.6	17.0									
		DTE	12:30	6.4	40		14.2	9.7	2.9	20.1	.9	1.06	18.3							1.96	.72	.017
		HTE	13:00	7.9	45		13.4	9.3	2.8	21.0	.7	.8	16.7							2.39	.76	.00003
		SCB	13:35	5.2	44		20.6	11.1	2.9	21.8	2.9	12.5	21.4							3.57	1.06	7.8
		LA	15:15	12.1	12	20.4	21.9	-	3.3	5.0	.3	.00	1.0	11.5	.28					.00	.10	0.0
		CLU	15:30	8.1	36	17.6	15.1	8.2	1.7	20.2	.2	.82	16.8	7.29	.01	.51	.83	6.62	.125	2.76	.74	.000007
		CLO	15:45	8.1	35		13.7	9.7	2.7	20.3	.3	.77	17.1							2.46	.70	.000006
		FB	15:30	-	-	39.6	-	-	-	-	-									-	-	-
		MW	15:15	8.8	12		.75	.34	1.0	.68	1.2	.00	1.1							.00	.02	0.0
1[3]	11-29	SCF	16:10	8.5	47	6.7	16.4	4.4	1.5	24.3	.51	.85	10.9	7.4	<.04	.77	.60	6.7	.090	3.03	.72	.000002
		UBD	15:45	5.1	48		22.2	5.5	1.5	25.0	2.33	13.5	10.6							3.68	.75	13.
		LBD	15:30	4.9	48		26.2	5.6	1.6	25.6	2.13	18.6	12.4							3.47	.91	28.
		DTE	16:40	6.4	39		16.8	4.7	1.6	25.0	.97	.57	10.3							1.35	.58	.007
		HTE	17:00	7.9	47		16.4	4.2	1.5	25.1	.53	.70	9.54							2.50	.65	.00002
		SCB	16:25	4.7	46		21.7	5.9	1.5	26.5	3.36	13.2	12.3							1.50	.81	30.
		CLO	11:00	8.5	34		16.2	4.9	1.6	23.6	.40	.47	11.1							1.77	.61	.0000005
		CLU	11:00	8.7	37	20.2	15.8	4.9	1.6	22.6	.30	.58	10.9	7.3	<.04	.82	.62	6.5	.095			
		LA	11:00	12.2	8	22.5	21.5	-	1.4	2.5	.40	0.0	1.0	11.0	<.04	1.44	<.01	.85	-	0.0	.10	0.0
		FB	11:00	-	-	37.0																

(Continued)

TABLE 3-2. CHEMICAL DATA SUMMARY (Continued)

Sample identification				Slurry properties			Liquid analyses (mmol/liter)							Solid analyses (mmol/g)						Computer results		
Test	Date	Stream[1]	Time	pH	Temp (°C)	% Solids	Ca^{++}	Mg^{++}	Na^{+}	Cl^{-}	$CO_3^{=}$	$SO_3^{=}$	$SO_4^{=}$	Ca^{++}	Mg^{++}	$CO_3^{=}$	$S.SO_4^{=}$[2]	T.S.	Ox Frac	$CaSO_3RS$	$CaSO_4RS$	$P*SO_2$(PPM)
1[3]	12-1	SCF	11:35	8.4	45	6.6	17.7	3.3	1.4	24.6	.5	.72	10.7	7.3	<.04	.61	.66	6.6	.100	2.70	.73	.000002
		UBD	11:15	5.1	47		23.5	4.4	1.4	24.5	2.2	13.1	11.8							3.76	.85	12.
		LBD	11:10	4.8	46		26.3	4.4	1.0	23.2	2.1	16.7	13.7							2.63	.99	29.
		DTE	12:05	7.5	44		17.9	3.6	1.4	24.5	.9	.63	10.6							2.28	.71	.0001
		HTE	12:15	8.2	46		17.8	3.4	1.0	24.3	.6	.68	10.2							2.52	.72	.000005
		SCB	11:40	4.9	45		24.9	4.8	1.2	25.7	3.1	14.6	13.1							2.84	.91	19.
		CLO	11:30	8.4	37		17.9	3.7	1.5	24.3	.4	.50	11.1							1.92	.66	.0000009
		CLU	11:30	8.6	36	19.8	18.0	3.5	1.1	24.6	.3	.30	11.2	7.1	<.04	.74	.64	6.6	.097	1.16	.67	.0000002
		MW	11:30	7.2	13		.84	.02	1.2	.35	1.2	0.0	1.1							0.0	.02	0.0
		FB	11:30	-	-	35.3																
2[3]	12-3	SCF	11:30	8.1	48		18.8	2.6	1.2	23.6	-	.59	11.8	7.3	<.04	.54	.69	6.8	.101	2.20	.89	.000008
		UBD	11:10	4.6	47		33.5	3.7	1.3	24.1	-	16.5	23.4							1.76	1.79	47.
		LBD	11:15	4.6	46		32.2	3.7	1.5	-	-	18.5	20.6							1.98	1.54	50.
		DTE	12:05	6.1	45		19.7	3.2	1.2	-	-	.74	13.3							1.28	.94	.037
		SCB	11:45	4.8	47		27.4	4.0	1.6	-	-	12.6	17.9							1.98	1.33	23.
3[3]		SCF	15:20	8.4	47	6.6	18.8	2.6	1.2	23.1	-	.58	11.0	7.3	<.04	.65	.60	6.8	.088	2.21	.83	.000002
		UBD	15:00	5.3	47		23.2	3.4	1.2	23.4	-	7.31	14.0							3.25	1.05	4.0
		LBD	15:05	5.2	47		27.7	3.5	1.2	-	-	13.3	16.3							5.00	1.24	9.1
		DTE	15:40	7.2	44		18.6	2.6	1.2	-	-	.58	11.1							2.05	.78	.0004
		SCB	15:25	4.8	46		26.8	3.9	1.4	-	-	11.7	17.7							1.86	1.29	20.
4[3]	12-6	SCF	10:40	6.8	48	6.6	15.3	2.6	1.9	22.0	-	1.16	7.00	7.5	<.04	.62	.56	7.0	.080	3.42	.52	.005
		UBD	10:15	4.8	47		23.0	2.8	1.5	22.0	-	16.1	9.8							2.44	.74	30.
		LBD	10:25	4.7	46		26.4	2.8	1.8	-	-	19.6	10.8							-	-	-
		DTE	11:20	4.0	43		14.8	2.5	1.8	-	-	1.18	8.46							2.70	.54	13.
		SCB	10:55	4.6	46		24.1	3.1	1.5	-	-	15.9	11.8							1.58	.86	46.
5[3]		SCF	16:00	9.0	48	6.6	15.3	2.6	1.5	21.5	-	1.15	6.37	7.4	<.04	.62	.49	6.9	.071	4.30	.47	.0000003
		UBD	15:40	4.5	49		21.5	2.1	2.0	22.0	-	12.9	8.9							.87	.71	62.
		LBD	15:45	4.8	49		24.0	2.1	1.5	-	-	17.0	10.4							2.54	.83	35.
		SCB	16:10	5.1	48		22.1	2.5	1.7	-	-	14.2	9.6							4.00	.73	14.
Line out[3]	12-9	SCF	15:00	8.3	46	3.3	17.9	3.1	2.2	19.9	-	.70	11.7							2.62	.82	.000003
		LBD	14:50	4.8	48	-	28.2	3.4	2.2	20.1	-	19.5	13.6							3.09	1.07	37.
Line out[3]	12-10	SCF	9:40	7.7	48	3.0	19.4	3.2	2.2	18.6	-	.65	12.5							2.38	.95	.00005
		LBD	9:25	4.6	49		30.7	3.5	2.0	19.6	-	18.8	15.3							1.99	1.25	57.
6[3]	12-12	SCF	12:10	8.0	47	3.0	18.2	4.0	2.0	19.4	-	.81	13.3	7.22	.21	.50	.95	6.45	.147	2.94	.92	.00002
		UBD	11:45	5.1	48		23.5	4.2	2.0	19.5	-	12.5	12.7							3.19	.95	13.
		LBD	11:45	4.8	48	2.9	27.6	4.6	2.0	19.8	-	17.6	14.9							2.44	1.13	38.
		DTE	12:45	8.4	43		18.8	4.1	2.0	19.7	-	1.12	13.1							4.18	.84	.000003
		HTE	13:10	7.9	46		17.7	4.0	1.9	19.8	-	1.12	12.9							4.03	.86	.00004
		SCB	12:20	5.0	45		26.7	4.6	2.0	20.5	-	13.3	15.7							3.33	1.12	14.
		LA	10:30	12.3	25	16.7	20.3	.10	3.7	4.54	-	.93	1.0	11.9	.14					4.08	.08	0.0
		CLO	10:30	5.6	42		21.4	4.2	2.0	19.3	-	1.46	16.7							1.09	1.09	.33
		CLU	10:30	6.9	25	18.5	20.9	4.3	2.0	18.8	-	1.00	14.4	7.25	.03	.45	.97	6.55	.148	3.56	.94	.0007
		MW	10:30	8.5	22		.66	.47	.68	.81	-	.04	.62							.08	.01	.0000001
		FB	13:30	-	-	40.6																

(Continued)

TABLE 3-2. CHEMICAL DATA SUMMARY (Continued)

Sample identification				Slurry properties			Liquid analyses (mmol/liter)							Solid analyses (mmol/g)						Computer results		
Test	Date	Stream[1]	Time	pH	Temp (°C)	% Solids	Ca^{++}	Mg^{++}	Na^{+}	Cl^{-}	$CO_3^{=}$	$SO_3^{=}$	$SO_4^{=}$	Ca^{++}	Mg^{++}	$CO_3^{=}$	S.$SO_4^{=}$[2]	T.S.	Ox Frac	$CaSO_3RS$	$CaSO_4RS$	P*SO_2(PPM)
6[4]	12-15	SCF	20:35	8.4	47	3.0	15.2	3.9	2.3	19.6	-	.72	10.6	7.24	.06	-	1.00	6.62	.151	2.58	.69	.000003
		UBD	20:20	4.9	48		22.2	4.2	2.3	18.9	-	13.1	13.7							2.27	.97	21.
		LBD	20:25	4.8	48		27.1	4.3	2.3	20.3	-	19.0	14.9							2.87	1.11	37.
		DTE	21:20	8.2	42		15.7	3.8	2.3	20.2	-	.80	11.7							2.92	.68	.000006
		HTE	21:45	8.1	46		16.5	4.0	2.5	20.3	-	.52	12.0							1.88	.79	.000007
		SCB	20:50	5.0	46		23.8	4.6	2.7	21.4	-	16.9	12.5							3.89	.86	19.
		LA	-	12.4	25	16.1	20.9	.23	3.4	3.81	-	.26	1.21	11.7	.18					1.1	.89	0.0
		CLO	21:00	5.5	33		19.2	4.3	2.7	12.7	-	5.12	14.1							3.60	.80	.87
		CLU	21:05	6.4	37	18.7	18.3	4.4	2.4	20.9	-	.72	13.9	7.28	.11	.56	.97	6.49	.149	1.74	.79	.008
		MW	-	8.4	15		2.78	.16	.65	.89	-	.01	.78							.04	.03	0.0
7[4]	12-20	SCF	18:45	7.9	46	6.9	12.4	3.2	2.7	22.7	.4	.72	7.51	7.4	<.04	.45	.69	6.64	.104	2.51	.46	.00003
		UBD	18:30	4.9	46		17.9	3.8	2.4	19.7	2.1	16.0	7.30							2.63	.48	24.
		LBD	18:30	4.7	48		20.4	3.8	2.9	19.8	2.0	18.7	9.8							1.99	.67	47.
		DTE	19:10	8.1	41		12.0	4.0	2.6	19.8	.6	1.30	6.46							4.55	.34	.00002
		HTE	19:35	8.2	44		11.2	2.8	2.3	20.1	.5	.35	7.43							1.24	.42	.000003
		SCB	19:00	4.7	46		18.0	4.0	2.4	20.9	3.6	16.0	12.5							1.55	.74	39.
		LA	19:05	12.4	15	19.0	21.2	.17	3.9	4.0	.24	.10	1.40							.46	.13	0.0
		CLO	19:00	8.2	36		11.5	3.0	2.7	20.0	.5	.46	7.58							1.69	.38	.000003
		CLU	19:05	8.9	31	22.2	11.3	2.8	2.7	19.4	.2	.50	7.72							1.88	.39	.0000009
		MW	20:00	8.4	15		.50	.04	.57	.69	1.01	.06	.59							1.11	.01	.0000002
7[4]	12-21	SCF	17:00	8.2	47	7.0	12.4	2.9	2.3	21.0	.5	.80	8.0	7.2	<.04	.69	.32	6.8	.047	2.72	.40	.00001
		UBD	16:30	5.0	49		20.1	3.5	2.3	20.8	2.1	17.1	7.5							3.08	.42	27.
		LBD	16:30	4.8	49		23.1	3.8	2.3	21.2	1.9	21.7	8.0							2.62	.51	53.
		DTE	17:40	10.5	39		16.8	4.0	2.3	20.7	.3	.78	8.7							2.82	.50	0.0
		HTE	18:00	7.9	45		12.4	3.3	2.4	20.9	.5	.73	7.8							2.43	.39	.00003
		SCB	17:15	5.3	45		19.6	4.3	2.5	21.8	3.5	16.5	8.6							5.9	.45	11.
		CLO	17:15	8.2	34		11.5	3.1	2.4	20.1	.4	.41	8.2							1.37	.39	.000005
		CLU	17:10	8.9	31	20.5	11.9	3.0	2.5	20.1	.3	.40	8.1	7.1	<.04	.70	.48	6.7	.072	1.37	.40	.0000002
8[4]	12-22	SCF	12:25	8.0	46	6.7	12.6	3.3	2.6	20.8	.6	.82	8.4	7.4	<.04	.60	.23	6.6	.035	2.74	.41	.00002
		UBD	12:05	4.6	48		26.8	3.9	2.5	21.4	2.0	27.7	8.1							2.56	.48	94.
		LBD	12:10	4.5	48		26.3	4.0	2.5	21.2	1.8	27.3	8.5							2.00	.50	120.
		DTE	12:55	6.1	38		13.9	3.6	2.5	21.5	1.3	2.7	8.4							3.70	.42	.20
		SCB	12:40	4.8	47		21.1	4.2	2.6	22.7	2.9	16.9	9.2							2.20	.51	37.
9[4]		SCF	16:15	8.0	47	6.7	12.4	3.3	2.5	21.9	.5	.95	8.3	7.2	<.04	.57	.25	7.0	.036	3.16	.40	.00003
		UBD	15:55	5.0	48		19.4	3.9	2.5	21.8	2.2	14.3	7.3							2.87	.41	20.
		LBD	15:55	4.8	48		23.1	3.9	2.5	22.1	2.3	20.9	9.4							2.81	.53	46.
		DTE	16:45	9.4	40		14.7	4.0	2.4	21.5	.5	.92	7.1							3.20	.38	.00000004
		SCB	16:25	4.8	47		19.3	4.0	2.5	22.2	3.1	14.4	9.1							1.81	.49	32.

---

[1] Stream Identification

SCF - Scrubber Feed
UBD - Upper Bed Downcomer
LBD - Lower Bed Downcomer
DTE - Draft Tube Effluent
HTE - Hold Tank Effluent
SCB - Scrubber Bottoms

LA - Lime Additive
CLU - Clarifier Underflow
CLO - Clarifier Overflow
FB - Filter Cake Bottoms
MW - Makeup Water

[2] Specific Sulfate

[3] The $SO_3^{=}$ values report for SCF and LBD streams were obtained from C.E. The others were estimated from the ratio of Radian sulfite to C.E. sulfite for these two streams.

[4] Radian obtained sulfite number using C.E. low pH method.

The Radian analysis technique yielded reported sulfite concentrations which were too high and the fact that Combustion Engineering's (C.E.) numbers appeared to be more reasonable led to a comparison of the two techniques. In the C.E. method, deionized water is adjusted to pH 1 with concentrated HCl, and a measured aliquot of I_2 is added. A filtered sample is pipetted into this solution, and the remaining I_2 is back titrated with $Na_2S_2O_3$. In the Radian sulfite method, a measured aliquot of I_2 is added to a solution which is buffered at pH 6 by a mixture of sodium acetate and acetic acid. A liquor sample containing sulfite is then added to the solution. The solution is weighed before and after the addition of the sulfite sample. The excess I_2 is back titrated with $Na_2S_2O_3$ to determine the amount of I_2 that reacted with sulfite. The two main differences between the Radian method and the C.E. method were the difference in pH and the absence of buffer in the C.E. method.

On-site experimentation indicated that the C.E. method yielded more reproducible and stable results. Therefore, on December 12, Radian began analyzing for sulfite using the C.E. method. Sulfite values reported here for dates prior to 12-15-76 were obtained by C.E. personnel. EPA Contract 68-02-2608-021 identified the interfering species present in carbide lime as thiosulfate and developed a technique for measuring sulfite which eliminates the interference (3).

4.0 DISCUSSION OF RESULTS

Material balance results generated in Phase I are given in Table 4-1. The methods used to calculate these numbers are presented in Appendix F.

Generally speaking, these material balances indicate that the flow rate and analytical data collected are resonably accurate. The "$\Delta SO_2(g)$" term is a gas phase measurement of the SO_2 which is absorbed by the scrubbing system. An independent measurement of the sulfur sorption can also be made by employing liquid flow rates and analytical data. The "Sulfur Sorption (liq)" term calculated from the liquid data agrees reasonably well with the gas phase SO_2 depletion. The liquid sorption numbers are generally about 10 percent lower which indicates a slight bias either in the gas or liquid data. For those cases where solid phase steady state had supposedly been achieved, the sulfur exit rate should be equivalent on a molar basis to the amount of SO_2 sorbed. In this phase, essentially all of the sorbed sulfur left the system as a solid, and the sulfur exit rates agree quite well with the other measures of the sulfur removal rate. These results indicate that the flow measurements and analytical data gathered in Phase I are within experimental accuracy.

The remainder of this section discusses some of the specific test results and observations for Phase I.

4.1 Base Case Operations

Base case testing included Tests 1 and 7. The system was operated in its normal flow configuration with carbide lime during the base case tests. Five different sample sets were taken during these two tests.

TABLE 4-1. MATERIAL BALANCE RESULTS (gmoles per minute)

Test	Date	$\Delta SO_2(g)$	$\Delta S(liq)$	$\Delta Ca(liq)$	Sulfur Sorption (liq)	Ca Solid In	Ca Solid Out	Lime Utilization(1)	S Solid Out	S Liq Out	Oxidation Rate	Oxidation Fraction(2)
1	11-22	278	387	160	244	283	317	.90	290	1.5	37	.127
1	11-29	247	358	171	203	387	248	.91	224	negl.	20	.090
1	12-1	242	372	164	224	288	241	.90	218	negl.	22	.100
2	12-3A	217	382	194	201	230	(3)	(3)	(3)	negl.	(3)	.101
3	12-3B	289	451	212	254	335	(3)	(3)	(3)	negl.	(3)	.088
4	12-6A	257	454	212	256	299	(3)	(3)	(3)	negl.	(3)	.080
5	12-6B	243	387	166	232	385	(3)	(3)	(3)	negl.	(3)	.071
6	12-12	208	343	176	186	280	256	.89	229	negl.	34	.147
6	12-15	241	436	216	238	225	257	.91	235	negl.	35	.151
7	12-20	299	415	150	280	295	328	.90	294	negl.	31	.104
7	12-21	237	423	202	232	247	313	.94	296	negl.	14	.047
8	12-22A	290	361	185	186	204	(3)	(3)	(3)	negl.	(3)	.035
9	12-22B	299	460	239	228	300	(3)	(3)	(3)	negl.	(3)	.036

(1) Lime Utilization = $\frac{\text{S Solid Out}}{\text{Ca Solid Out}}$

(2) Oxidation Fraction = Sulfate Out/Sulfur Out

(3) Solid phase line out was not achieved for the short term L/G and pH tests. Thus, these values would not be indicative of steady state operation.

During base case operation, inlet gas SO_2 concentrations ranged from 2370 to 3030. Outlet gas SO_2 concentrations varied between 470 and 930 ppm. The resulting SO_2 removal efficiencies ranged between 66 and 81 percent with 74 percent removal being about average.

Operation with carbide lime led to oxidation fractions (measured by the sulfate/total sulfur ratio in the solid phase) which were generally about 0.1. Earlier investigation has shown that the solid sulfate/total sulfur fraction is related to the gypsum relative saturation in the liquor from which the solids are precipitated (1). This study indicated that for sulfate/total sulfur ratios less than approximately 0.16, all of the precipitated sulfate will be incorporated as a solid solution with calcium sulfite and the liquor should remain subsaturated with respect to gypsum.

This relationship between oxidation fraction and gypsum relative saturation was verified during base case operation. Oxidation of 10 percent or less of the absorbed SO_2 led to gypsum relative saturations of between 0.5 and 0.75 in the hold tank effluent or scrubber feed stream liquor. As expected, no gypsum solids were identified, and the sulfate formed during Phase I was purged from the system as a calcium sulfite-sulfate solid solution. This is shown by the I.R. scan presented in Figure 4-1. The triplet peak in the 1100 to 1300 (cm^{-1}) range here indicates the presence of calcium sulfite-sulfate solid solution and no gypsum. This result is consistent with the low oxidation and gypsum subsaturated conditions noted in the hold tank during Phase I.

Significant amounts of calcium solids were dissolving in the scrubber during Phase I. This can be seen in the $Ca_{(liq)}$

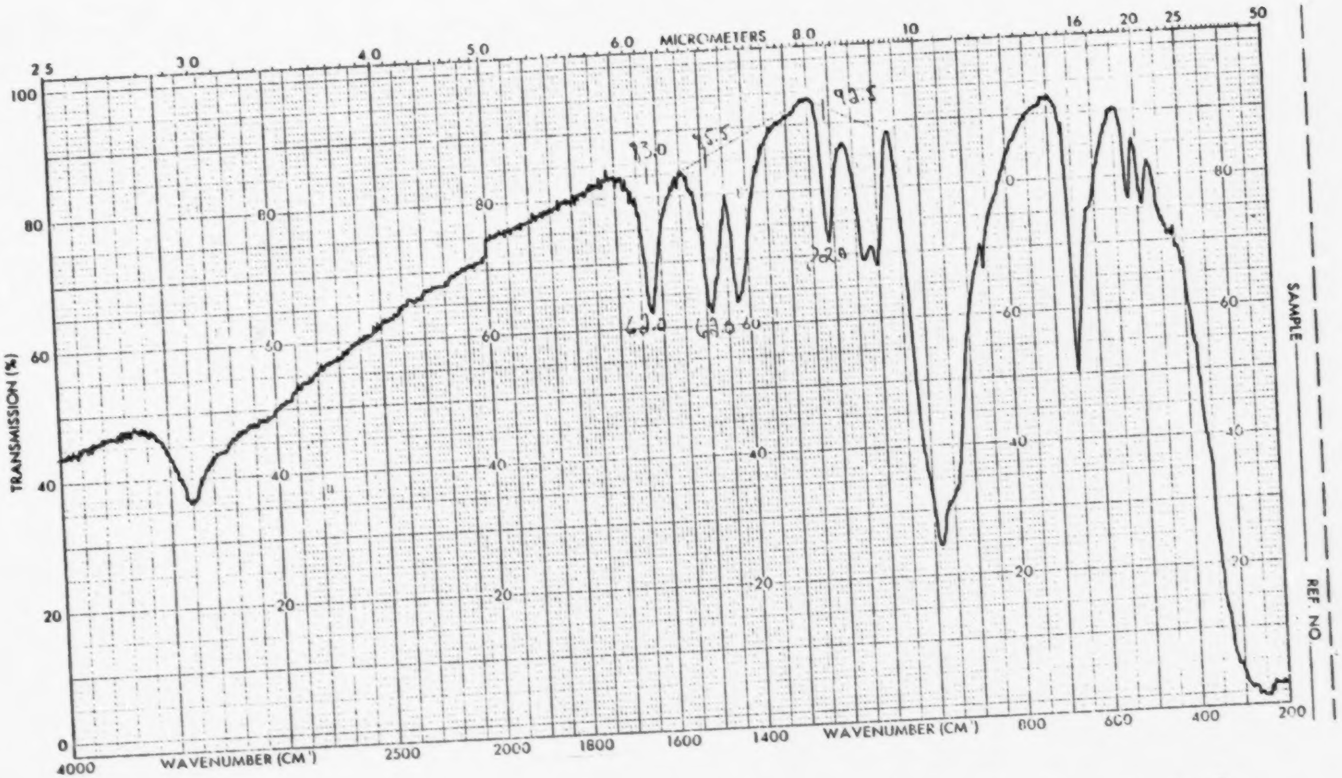


Figure 4-1. Infrared scan for solid sample taken 11-22-76 - Phase I.

values from Table 4-1 and from the rate summaries for Test 1 which are presented in Tables 4-2, 4-3, and 4-4. Since no calcium hydroxide solids were present in the recirculating slurry, the calcium increases resulted from dissolution of the calcium sulfite-sulfate-carbonate solid solution on the marble beds.

As Tables 4-2 through 4-4 indicate, the calcium sulfite dissolution provided from 1/3 to 1/2 of the alkalinity required for the SO_2 sorption which occurred during Phase I. As the liquid phase alkalinity was consumed, the scrubbing liquor pH dropped, and the relative saturation of calcium sulfite dropped below 1.0 in areas burdened with high SO_2 loadings. (Computer runs indicate that the downcomer streams were supersaturated with respect to $CaSO_3$, but these streams represent average conditions of liquor on the beds.) When the liquor was subsaturated, calcium sulfite dissolved which provided additional alkalinity for SO_2 absorption. The relatively large amount of alkalinity which was derived from the solids in this system was due to the long slurry residence time (∿30 seconds) on the marble beds and the relatively low L/G's employed.

In addition to the alkalinity it provided, the calcium solids dissolution was also the major cause of the increase in gypsum relative saturation measured across the scrubber. Increases in liquid phase Ca^{++} and $SO_4^{=}$ ions led to increases of about 30 percent in gypsum relative saturations across the lower bed during base case testing. It can be seen from Table 3-1 that the calcium concentration increased about 60 percent on the lower marble bed compared to a sulfate concentration increase of less than 20 percent. Thus, the calcium dissolution was the major contributor to the increased gypsum relative saturation.

TABLE 4-2. CHEMICAL REACTION CALCULATION SUMMARY

Test No. 1 Sample Set No. 1 Date 11-22-76	Reaction Rate (g-moles/min)					
	Scrubber	Holding System				Total System
		Draft Tube	Hold Tank	Surge Tank	Total	
SO_2 Sorption	268	--	--	--	--	268
Oxidation	--	--	--	--	--	35
Total Sulfur Precipitation	-118	340	42	6	388	270
Calcium Carbonate Precipitation	--	28	5	2	35	--
Calcium Hydroxide Dissolution	--	224	28	7	259	259

TABLE 4-3. CHEMICAL REACTION CALCULATION SUMMARY

Test No. 1 Sample Set No. 2 Date 11-29-76	Reaction Rate (g-moles/min)					
	Scrubber	Holding System				Total System
		Draft Tube	Hold Tank	Surge Tank	Total	
SO_2 Sorption	252	--	--	--	--	252
Oxidation	--	--	--	--	--	22
Total Sulfur Precipitation	-106	378	13	-32	359	253
Calcium Carbonate Precipitation	--	42	10	0	52	--
Calcium Hydroxide Dissolution	--	257	14	-32	239	239

The method of calculation is presented in Appendix F.

TABLE 4-4. CHEMICAL REACTION CALCULATION SUMMARY

Test No. 1 Sample Set No. 3 Date 12-1-76	Reaction Rate (g-moles/min)					
	Scrubber	Holding System				Total System
		Draft Tube	Hold Tank	Surge Tank	Total	
SO_2 Sorption	242	--	--	--	--	242
Oxidation	--	--	--	--	--	--
Total Sulfur Precipitation	-130	376	8	-12	372	242
Calcium Carbonate Precipitation	--	31	6	3	40	--
Calcium Hydroxide Dissolution	--	249	12	-11	250	250

The method of calculation is presented in Appendix F.

During Phase I, the increase in gypsum relative saturation did not create a problem. Since the scrubber feed stream's gypsum relative saturation was generally less than 0.75, a 30 percent increase did not lead to supersaturated conditions in the scrubber. However, the importance of maintaining low oxidation and scrubber feed relative saturations while operating in this flow configuration is emphasized. Should the gypsum relative saturation exceed 1.3 to 1.4 in the scrubber, the chances of scale formation are greatly enhanced.

The dissolution of calcium/sulfur salts in the scrubber leads to increased sulfur precipitation in the reaction tank system. Although the net sulfur precipitation in the system is approximately equal to the amount of SO_2 absorbed in the scrubber, the actual precipitation occurring in the reaction vessels is about 50 percent higher. This result is shown in the reaction rate summaries (Tables 4-2 through 4-4).

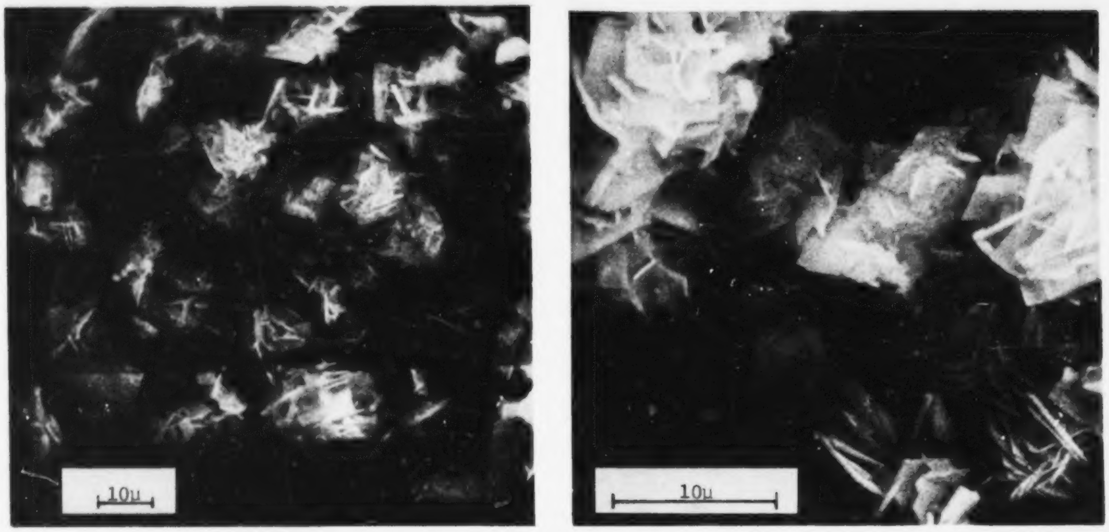
The reaction summaries also reveal useful information about the draft tube, a vessel some have believed is the key to this system's success. It can be seen from Tables 4-2, 4-3, and 4-4 that a large majority of the solid-liquid mass transfer which occurs in the hold tank actually happens in the draft tube. About 90 percent or more of the calcium sulfite-sulfate solid precipitation which occurred in the holding system was attributed to the draft tube. In addition, lime dissolution appeared to be rapid with greater than 90 percent of the dissolution occurring during the 30 second residence time in the draft tube. These results indicate that operation with a reduced hold tank volume should be possible.

Electron micrographs of representative solid samples gathered during Phase I are shown in Figure 4-2. Basically, the crystal structures appear to be rosettes which are typical of solids produced in lime systems.

4.2 L/G Tests

Low and high L/G sensitivity tests, Tests 2 and 3, were conducted on 12-3-76. At a low L/G, 5.2 ℓ/Nm^3, the SO_2 removal efficiency was 64 percent. With the L/G increased to 10.4 ℓ/Nm^3, the system's removal efficiency increased to 81 percent. These results compare to an average L/G of ∿7.5 ℓ/Nm^3 and 73 percent removal. This first L/G test series indicated that increasing L/G increases removal efficiency. This trend is one which would be expected. As the L/G increases, the gas is exposed to more liquid phase alkalinity and increased removal should result.

These same L/G changes were duplicated in Tests 8 and 9 which were conducted on 12-22-76. The results here indicated a different trend. A removal of 84 percent was achieved at an L/G



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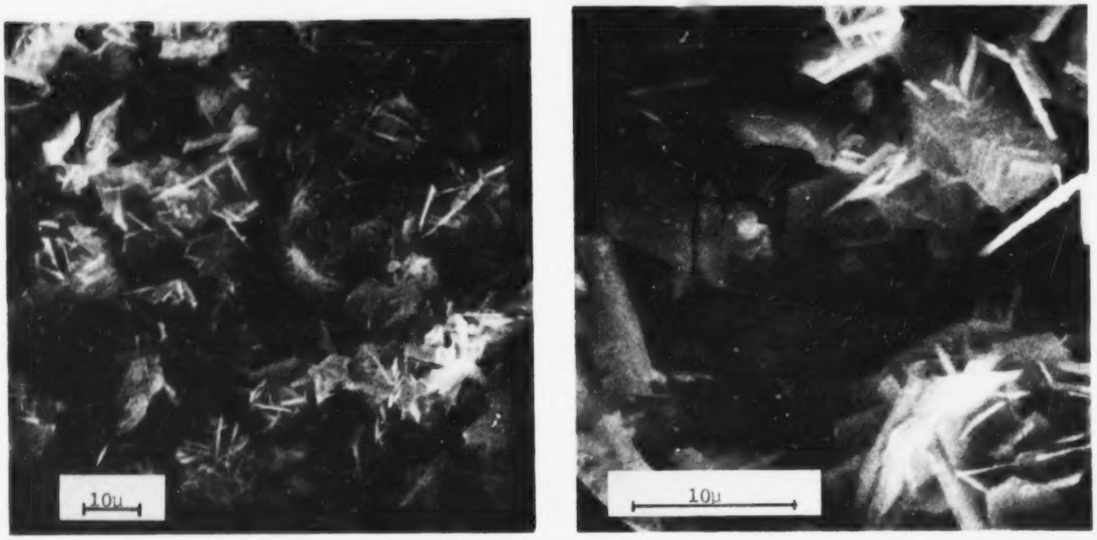

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Figure 4-2. Electron micrographs for Phase I scrubber feed solids.

of 5.2 ℓ/Nm^3 while 74 percent removal was obtained at an L/G of 9.5 ℓ/Nm^3. It was noted that the inlet SO_2 concentration was fluctuating widely on 12-22-76. This may have affected the results. Since the system conditions were changing, it is felt that the results from the second set of L/G tests did not document the actual effect of L/G on system operation.

4.3 pH Tests

Tests 4 and 5, conducted on December 6, 1976, tested the effect of scrubber feed pHs of 6.8 and 9 on system operation. No major difference was seen in scrubber performance due to the different pHs. SO_2 removal efficiencies were about 70 percent for both tests. The increase in pH should tend to increase liquid phase alkalinity. For instance a slightly larger fraction of sulfite will exist as alkaline $SO_3^=$ at pH 9.0 than at pH 6.8. An increase in liquid alkalinity should decrease the amount of solid alkalinity required for a specified SO_2 removal. However, the magnitude of the increase in these tests was not significant enough to indicate major differences in system chemistry.

4.4 Low Solids Test

On December 7, the clarifier feed rate was increased to reduce the solids concentration in the recirculating slurry. The slurry solids concentration reached its lower operating limit of three weight percent on 12-12-76. A further decrease in the solids level was not possible because the clarifier overflow return lines would not return enough water to the system.

The average SO_2 removal efficiency for this low solids test period was about 74 percent. This is approximately the same efficiency achieved during base case operation. However, the oxidation fraction rose to 0.15. The gypsum relative saturations for the scrubber feed and lower bed downcomer streams were 0.7-0.9 and 1.11-1.13 respectively. These were the highest steady-state values measured during Phase I.

To determine the significance of these increases, the difference in operation between the base case tests, Tests 1 and 7, should be considered. Test 1, which was conducted from 11-22 to 21-1-76, showed oxidation fractions of 0.090 to 0.127. The scrubber feed gypsum relative saturation ranged from 0.72 to 0.74, while the lower bed downcomer relative saturations ranged from 0.91 to 0.99. During Test 7, the oxidation fraction dropped to about 0.04. The ranges in gypsum relative saturation for the scrubber feed and lower bed downcomer streams were 0.40 to 0.46 and 0.51 to 0.67, respectively. Although the system was operating essentially at the same base case conditions, the difference in the oxidation recorded for Tests 1 and 7 is significant. Based on this comparison, it is difficult to attribute the increased oxidation observed in Test 6 solely to the reduced solids content in the recirculating slurry. Fluctuations in the system's process chemistry could also account for the observed changes.

4.5 Open Loop Operation

During Tests 7, 8, and 9, open loop operation was observed. The weight percent solids in the carbide lime feed was lower than during previous operation and blowdown was necessary to control the liquid level in the system. This blowdown rate was not measured by operating personnel. However, subsequent measurements made during Phases II and III indicated that about 75 liters per minute of blowdown was necessary to operate with roughly 10 weight percent solids in the lime additive stream. The amount of sulfur exiting in the liquor blowdown is small compared to the total sulfur leaving the system with the waste solids. More importantly, the soluble sulfate leaving in this stream is estimated to be only 5 percent of the total sulfate being formed in the system during this phase. Thus, the increased blowdown did not substantially affect the calculated oxidation rate or the system's operation.

APPENDIX B

PHASE II

COMMERCIAL LIME OPERATION

1.0 SUMMARY

The objective of Phase II was to study operation of the Paddy's Run system with commercial lime. The same process flow configuration was employed in this phase as in Phase I.

After operating the unit for about one month, it was concluded that the Paddy's Run FGD system could not be operated successfully in its base case configuration with commercial lime additive. This was due to a combination of 1) the differences between commercial and carbide lime in terms of their impact upon the process chemistry and 2) the mechanical limitations of the Paddy's Run system.

The oxidation fraction for commercial lime operation ranged between 0.15 and 0.21. This oxidation fraction is double that seen throughout the majority of Phase I operation. The inlet SO_2 concentration during Phase II ranged between 2500 and 3000 ppm while the removal efficiency was generally about 75 percent. These values are comparable to those observed in Phase I.

Throughout the majority of Phase II, the scrubber feed liquor remained slightly subsaturated with respect to gypsum. More specifically, the scrubber feed relative saturation varied between 0.8 and 1.0. However, due to increases in calcium and sulfate ion concentrations, the liquor on the marble beds became supersaturated with respect to gypsum. As a result, gypsum scale was deposited over most of the internal surfaces in the scrubber.

Changes were made in the scrubber feed rate and the recirculating slurry solids content in an attempt to eliminate the scale problem. Neither of these changes had a noticeable effect on the rate of scaling in the system.

The details of Phase II operation are presented in the remaining sections of this technical note. Section 2.0 describes the test approach employed, Section 3.0 summarizes the results obtained, and Section 4.0 discusses the implications of these results.

2.0 TEST APPROACH

Essentially the same tests which were conducted in Phase I were planned for Phase II. However, while operating in its normal process configuration (Figure 2-1), severe gypsum scaling in the scrubber was observed. Therefore, the entire Phase II effort was devoted to documenting commercial lime process chemistry and to making the system operable. These changes included increasing the scrubber feed liquor rate and increasing the recirculating slurry solids content.

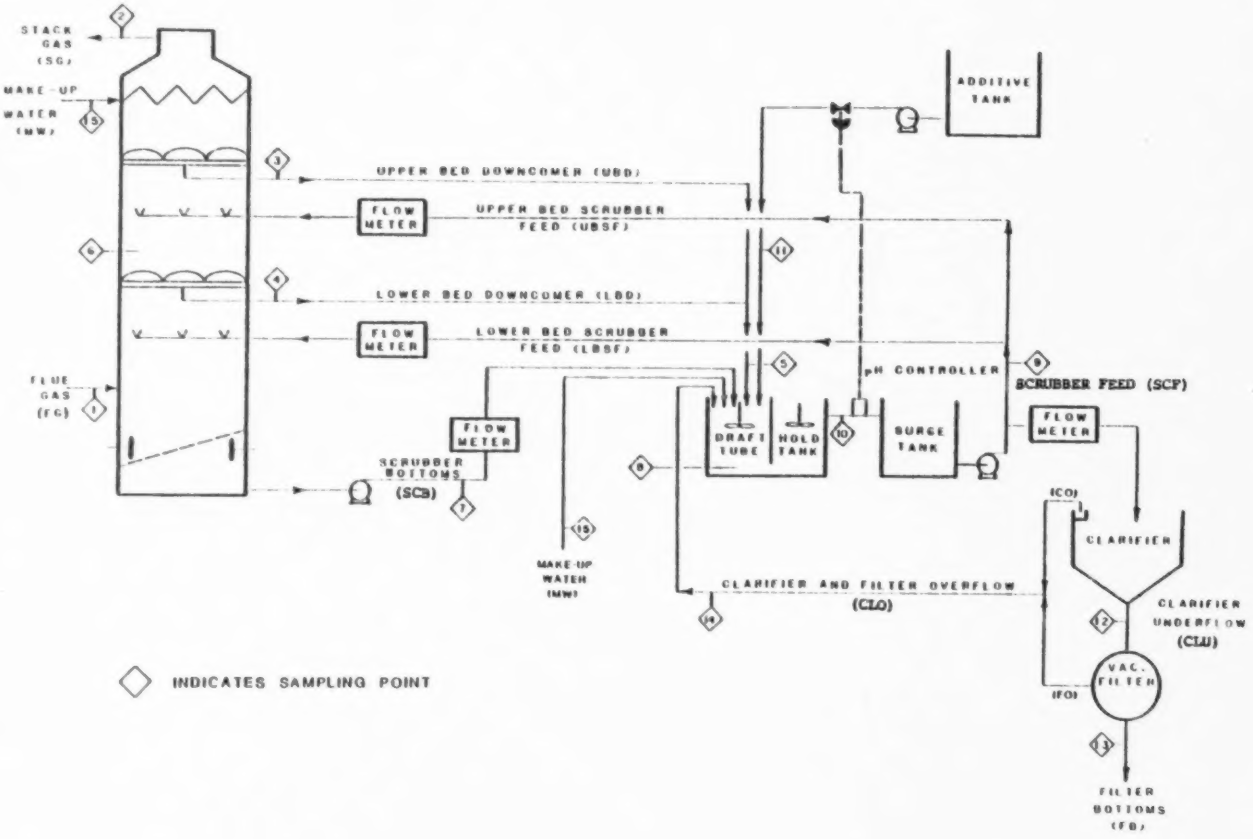

STACK GAS (SG)
2
MAKE-UP WATER (MW)
15
3
UPPER BED DOWNCOMER (UBD)
FLOW METER
UPPER BED SCRUBBER FEED (UBSF)
6
4
LOWER BED DOWNCOMER (LBD)
FLOW METER
LOWER BED SCRUBBER FEED (LBSF)
11
5
FLUE GAS (FG)
1
FLOW METER
SCRUBBER BOTTOMS (SCB)
7
15
MAKE-UP WATER (MW)
8
DRAFT TUBE
HOLD TANK
10
pH CONTROLLER
SURGE TANK
ADDITIVE TANK
9
SCRUBBER FEED (SCF)
FLOW METER
(CO)
CLARIFIER
CLARIFIER AND FILTER OVERFLOW (CLO)
14
CLARIFIER UNDERFLOW (CLU)
12
VAC. FILTER
(FO)
13
FILTER BOTTOMS (FB)
INDICATES SAMPLING POINT

Figure 2-1. Commercial lime testing configuration.

3.0 RESULTS

The process and analytical results obtained during Phase II are presented in this section. Figure 3-1 summarizes important process and analytical data gathered during Phase II. More detailed process and analytical results are reported in the following two subsections.

3.1 Process Data

As can be seen from Figure 3-1, system operation in Phase II was characterized by a series of scrubber outages. Table 3-1 explains the reason for each outage. A large amount of maintenance was necessary to keep the system operational. Of particular note here are the leaks which occurred in the walls of the B module of the scrubber. Some of the erosion which caused the leaks may have been due to higher slurry solids concentrations employed during part of Phase II. However, most of the leaks were a result of normal wear on scrubber walls or possible increased wear on the walls due to nozzle failure. The increased frequency of scrubber inspections was directly related to the scaling problems.

TABLE 3-1. PHASE II OUTAGES

Date	Hours Off-Line	Reason
3-10	4.6	I.D. Fan Balancing and Cleaning
3-14	4.0	Scrubber Inspection
3-16	6.5	Screen Repairs
3-21 → 3-30		Purge Sulfite Interference
3-31	6.3	Generator Problem
4-1	1.7	Scrubber Patchwork
4-2	2.6	Scrubber Patchwork
4-3	1.5	Scrubber Patchwork
4-4	2.0	Scrubber Inspection
4-6	2.6	Scrubber Inspection
4-7	6.0	Switch to "A" Module
4-8	3.7	Scrubber Patchwork
4-10	4.5	High River Level-Plugged Condenser
4-11	1.2	Scrubber Inspection

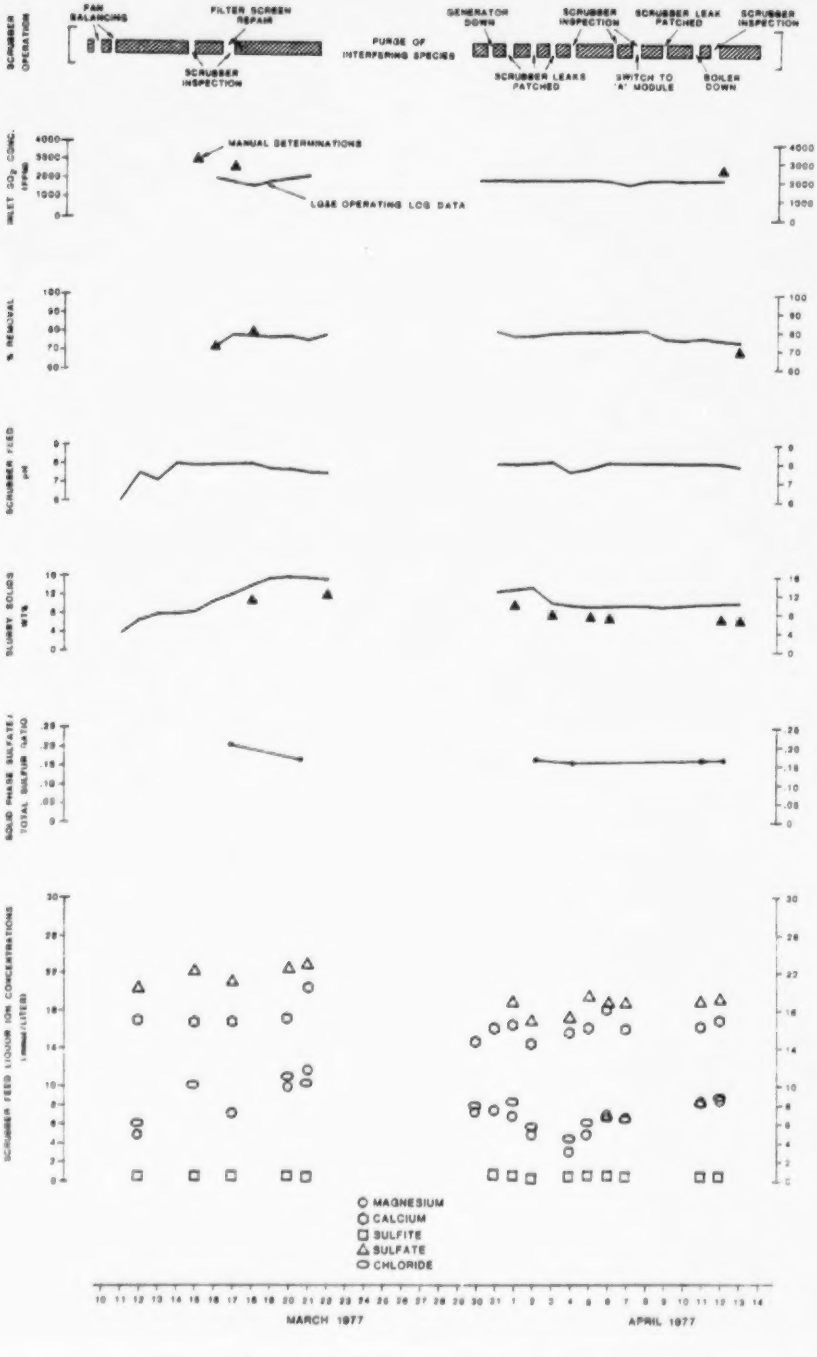


Figure 3-1. Process and operating data for Phase II commercial lime testing.

Phase II scrubber operation began on 3-10-77 with Module B in service. Process measurements for Phase II are detailed in Table 3-2. Early analytical results indicated that conditions conducive to gypsum scale formation were present on the marble beds. Scale formation was confirmed by visual inspection on 3-14-77. In an effort to reduce the rate of scale deposition, the recirculating slurry solids concentration was increased from about 7 percent to 12 percent. However, this did not significantly reduce the rate of scale buildup.

The scrubber feed rate was increased from 22,700 to 26,550 liters/min (6000 to 7000 gpm) on 3-17-77. This was done to reduce the scaling potential of the liquor on the marble beds. However, no indication of a major change in scaling potential was noted either in the analytical results or upon scrubber inspection.

On 3-21-77, the system was shutdown to purge a species which interfered with Radian's sulfite analytical technique. While this will be discussed further in Section 3.2, the source of this interference was the AIRCO process water which was contaminated with carbide lime impurities.

After cleanout, the system (Module B) was restarted on 3-30-77 and operated until 4-7-77. During this period, the liquor on the marble beds remained supersaturated with respect to gypsum and scale continued to build up on the beds. In addition, the sidewalls of the scrubber began to develop leaks. These leaks were a result of erosion through the protective scrubber lining at points where slurry was being sprayed on the walls. This erosion was most severe in places where nozzles close to the wall became detached and the walls were sprayed with a direct stream of concentrated slurry. Once the protective scrubber lining was destroyed, corrosion of the carbon steel

TABLE 3-2. PHASE II - PROCESS MEASUREMENTS

	Base case commercial lime Test #10 March 13	March 15	Increase L/G and % solids Test #11 March 17	Decrease % solids Test #12 April 11	Test propensity for scaling on clean scrubber Test #13 April 12
Flue gas (Nm^3/hr) (dry)	177,000	-	-	-	193,000
SO_2 Inlet ppm	-	3,070	2,640	-	2,550
SO_2 Outlet ppm	-	845	526	-	787
Removal efficiency (%)	-	72.4	80.1	-	69.1
Scrubber feed (ℓpm)	22,700	→	26,500	→	26,100
Upper bed	11,400	→	13,300	→	13,200
Lower bed	11,300	→	13,200	→	12,900
L/G (ℓ/Nm)	7.69				8.11
Feed pH	8.1	8.0	8.9	8.2	8.5
Recirculating solids content (%)	∿ 7	-	10.9	8.0	6.8
Scrubber bottoms (ℓpm)	-	-	-	-	3,780
Clarifier feed (ℓpm)	617	-	-	-	484
Clarifier overflow (ℓpm)	-	-	-	316	417
Lime additive (ℓpm)	-	-	-	-	116

Notes: Lower and upper bed downcomer flow rates were estimated from marble bed prototype data - the slurry reject from each bed was equal to the scrubber bottoms flow.

scrubber walls was possible and leaks resulted. Since the increased slurry solids had not significantly reduced the scaling potential of the scrubbing liquor, the solids concentration was lowered back to its normal operating level. The slurry's erosion potential was reduced at this lower solids level.

On 4-7-77, Module B was shut down and Module A was started up. This decision was based on two factors. First, further operation of Module B was impractical due to the maintenance problems. Second, a shift in operation to Module A was planned to determine if the scaling observed in Module B was due to operating conditions established during start-up. Although a composite sample of the scrubber effluent indicated supersaturated conditions were present in the scrubber, the "average" relative saturation was below the level generally recognized as critical for scaling.

Module A was operated for seven days. The system continued to operate supersaturated with respect to gypsum and inspection on 4-11-77 again showed scale buildup. The system was operated until 4-14-77 to satisfy load demand. At that point the system was shut down due to continuing scale formation.

Throughout Phase II, the SO_2 removal efficiency remained between 69 and 80%. The average removal was approximately 75%. Manual samples showed inlet SO_2 concentrations from 2500 to 3000 ppm.

Throughout Phase II, the thickener overflow periodically was routed to the sewer to control liquid level in the system. Since this flow is not routinely monitored by unit operators, a precise flow rate cannot be determined. However, it appears from measurements made during Phase III that an average rate of 75 liters per minute is a reasonable estimate. The liquor blowdown

TABLE 3-3. CHEMICAL DATA SUMMARY

Sample identification				Slurry properties			Liquid analyses (mmol/liter)							Solid analyses (mmole/g)						Computer results		
Test	Date	Stream[1]	Time	pH	Temp (°C)	% Solids	Ca^{++}	Mg^{++}	Na^{+}	Cl^{-}	$CO_3^{=}$	$SO_3^{=}$	$SO_4^{=}$	Ca^{++}	Mg^{++}	$CO_3^{=}$	$S.SO_4^{=2}$	T.S.	Ox Frac	$CaSO_3RS$	$CaSO_4RS$	P^*SO_2(PPM)
10	3-12	SCF	-	8.0	51	-	17.0	5.2	7.2	6.3	-	.4	20.3							1.34	.97	.00001
	3-15	SCF	-	-	-	-	17.1	-	-	-	-	.4	22.4									
		UBD	-	-	-	-	30.2	-	-	-	-	14.6	24.7									
		LBD	-	-	-	-	26.3	-	-	-	-	21.9	25.5									
11	3-17	SCF	12:00	8.9	49	10.9	16.9	7.2	9.8	10.2	-	.58	21.3	7.14	.09	.39	1.42	6.77	.210	1.82	.89	.0000003
		UBD	11:40	4.8	50	-	23.7	7.3	9.5	10.8	-	13.5	23.5							1.61	1.10	30.
		LBD	11:05	4.9	51	-	26.6	8.5	8.6	10.6	-	19.3	24.4							2.96	1.16	33.
	3-20	SCF	13:00	7.9	47	-	17.4	10.1	8.7	11.1	-	.75	22.4							2.21	.91	.00003
		LBD	13:30	4.6	49	-	27.1	10.2	8.7	11.5	-	23.6	24.9							1.61	1.10	30.
	3-21	SCF	9:20	7.9	47	12.0	20.5	11.7	9.5	-	-	.5	22.8	6.88	0.0	.37	1.11	6.61	.168	1.51	1.01	.00002
		LBD	9:30	4.8	51	-	27.1	9.2	7.5	-	-	21.0	25.8							2.55	1.20	45.
12[2]	3-30	SCF	14:25	8.5	45	-	14.6	7.1	5.6	8.0	-	-	-	7.26	0.0	.37	-	6.77				
		LBD	14:25	4.9	48	-	21.6	6.1	4.8	6.6	-	22.0	-									
	3-31	SCF	16:25	8.2	47	10.3	16.2	7.5	4.8	-	-	.43	-									
		LBD	16:25	4.6	50	-	21.1	5.8	3.8	-	-	23.9	-									
		LA	16:25	-	-	11.2																
	4-1	SCF	-	8.5	45	-	16.5	6.7	3.4	8.4	-	.5	19.0							1.70	.89	.000001
		LBD	-	4.8	48	-	27.8	7.3	3.4	7.9	-	21.4	23.4							2.61	1.22	47.
	4-2	SCF	13:15	8.2	48	8.0	14.6	4.8	2.1	5.8	-	.1	16.9	7.12	.31	.43	1.15	6.88	.167	.34	.81	.000001
		LBD	13:45	4.8	49	-	26.9	5.4	2.6	5.9	-	18.9	23.2							2.28	1.25	44.
	4-4	SCF	9:00	8.9	47	7.9	15.8	2.9	1.4	4.4	-	.4	16.9	7.30	0.0	.62	1.03	6.74	.153	1.46	.88	.0000001
		LBD	9:30	4.8	49	-	25.3	3.2	1.3	4.0		18.0	20.9							2.42	1.17	38.
	4-5	SCF	12:55	7.8	47	7.7	16.2	5.1	1.5	6.1	-	.5	19.8							1.68	.94	.00004
		LBD	13:10	4.6	46	-	27.3	5.8	1.6	6.1	-	20.3	21.8			.53				1.70	1.20	66.
	4-6	SCF	10:00	8.3	48	-	18.3	7.3	1.7	6.8	-	.4	19.1							1.31	.94	.000002
		LBD	10:20	4.8	48	-	28.1	6.5	1.6	7.9	-	19.3	22.7							2.73	1.24	37.
	4-7	SCF	8:50	8.7	48	-	16.1	6.8	1.6	6.5	-	.4	19.0							1.34	.89	.0000004
		LBD	9:05	4.7	51	-	26.0	6.9	1.6	6.8	-	21.0	21.3							2.13	1.10	60.
	4-11	SCF	9:00	8.1	50	6.5	16.5	8.3	1.7	8.2	.6	.2	18.9	7.24	.13	.44	1.11	6.79	.163	.64	.87	.000003
		LBD	9:20	4.7	50	-	29.3	8.3	1.8	10.3	1.0	19.0	23.5							2.11	1.27	50.
		SCF	16:00	8.4	48	-	17.9	7.8	-	8.6	-	.4	19.3							1.34	.94	.000001
		LBD	16:20	4.5	50	-	31.8	7.4	-	9.7	-	24.4	21.2							1.84	1.21	100.
	4-12	SCF	10:30	8.5	49	6.8	17.1	8.1	1.4	8.8	.6	.5	19.4	7.28	.19	.53	1.11	6.79	.163	1.65	.91	.000001
		UBD	10:00	5.0	50	-	24.1	8.8	1.4	9.1	1.7	13.6	21.6							2.67	1.08	18.
		LBD	10:15	4.8	50	-	33.1	10.2	1.7	9.4	1.9	22.2	22.1							2.99	1.25	49.
		DTE	11:30	7.5	50	-	21.1	2.5	1.3	9.1	-	.2	19.2							.72	1.15	.00005
		SCB	11:00	4.7	49	-	26.7	9.0	1.6	10.0	2.0	24.6	20.1							2.57	1.01	63.
		LA	14:00	12.5	28	9.4	18.6	0.0	.7	.8	.3	.06	.15	12.4	0.0					.25	.01	0.0
		CLO	14:00	8.5	28	-	16.6	7.8	1.6	12.2	.8	.03	20.3							.11	.99	.00000002
		CLU	14:00	10.2	28	24.7	17.0	7.0	1.5	8.1	.2	.28	19.5	7.26	0.00					1.04	1.00	0.0
		MW	14:00	7.5	28	-	.1	0.0	.2	.3	1.0	.02	.46							.02	.01	.00001
		FB	14:00	-	-	39.1	-	-	-	-	-	-	-							-	-	-
		LBS	10:45	4.7	50	-	27.4	8.8	1.5	9.4	1.9	19.9	23.1							2.10	1.19	53.

[1] Stream Identification

SCF - Scrubber Feed	LA - Lime Additive
UBD - Upper Bed Downcomer	CLO - Clarifier Overflow
LBD - Lower Bed Downcomer	CLU - Clarifier Underflow
DTE - Draft Tube Effluent	MW - Makeup Water
SCB - Scrubber Bottoms	LBS - Lower Bed Sample

[2] Eliminated interfering species

was necessary because the lime solids concentration in the additive stream had fallen to 10-12 percent from the normal design level of 20-25 percent. This was because thickener employed at AIRCO was oversized for the service required. The lime solids inventory maintained in the thickener was insufficient to achieve 20 percent solids in the underflow. Thus, the lime solids concentration in the additive slurry entering the scrubbing system was inadequate for closed-loop operation.

3.2 Analytical Data

Table 3-3 presents the liquid and solid phase results from Phase II. Of particular note are the gypsum relative saturations of the scrubber feed and effluent streams. The relative saturation of the scrubber feed ranged from .81 to 1.01. The lower bed downcomer liquor was supersaturated throughout the test period with gypsum relative saturations ranging from 1.10 to 1.27. The oxidation fraction which was determined from solid phase measurements, ranged from 0.15 to 0.21. As mentioned previously, significant scale deposits were noted in the scrubber.

During Phase II start-up, an interference with Radian's analytical sulfite method was once again observed. This interference was similar to that noted during Phase I. To determine the effect of this interference on system operation, the source had to be identified and eliminated.

The source of the interference was traced to the water used to slake the commercial lime. This water was being contaminated by the thickener overflow stream from the carbide lime thickener. The contamination source was eliminated, and the scrubbing liquor was purged from the system to remove the remaining interference. These actions were taken during the shutdown between 3-21-77 and 3-30-77. Other than reducing the analytical problems, this action did not seem to significantly affect the chemistry of the system.

4.0 DISCUSSION

The major conclusion of the Phase II tests is that operation of the Paddy's Run FGD system in its normal flow configuration with commercial lime as the only additive is not feasible. Gypsum scale buildup occurred at such a rate that scrubber operation became impractical. Other aspects of the system's operation, such as SO_2 removal efficiency, were not significantly different from those encountered in carbide lime operation. The important process chemistry aspects of the commercial lime operation are discussed later in this section.

Due to the scaling conditions present in the scrubber, the major effort expended in Phase II was toward making the system operable and tracking its daily operation. The scrubber feed and lower bed downcomer streams were sampled frequently. Major changes in the system's chemistry are reflected in the compositions of these streams. In addition to these abbreviated sample sets, one full set of samples was collected (on 4-12-77) for material balance purposes.

To highlight the important aspects of the system's operation with commercial lime, this section includes discussions concerning the causes of gypsum scaling, effects of L/G and slurry solids concentration, the implications of the material balance calculations, and the nature of the solid crystal structures formed.

4.1 Gypsum Scaling

The major difference between Phase I and Phase II operation was the fraction of absorbed SO_2 which was oxidized to sulfate. Generally, the oxidation fraction in Phase I was 0.08 to 0.10. In Phase II, the oxidation fraction was in the 0.15 to 0.17 range.

The reduced oxidation with the carbide lime additive demonstrates a significant difference in the process chemistry between the two additives. This difference is also reflected by the interference with Radian's sulfite analytical technique which was experienced during carbide lime testing. The significance of this interference and its impact on the process chemistry was investigated under EPA Contract Number 68-02-260-021.(3) The cause of the interference is due to the presence of thiosulfate which also resulted in the decreased sulfite oxidation rates measured during Phase I.

The increase in oxidation rate in Phase II caused an increase in the liquid phase sulfate level and gypsum relative saturation of the reaction tank effluent (scrubber feed) slurry. During Phase I, the oxidation fraction remained below 10 percent and the scrubber feed stream's gypsum relative saturation was generally below 0.7. During Phase II, when the oxidation fraction was about 0.15, the scrubber feed liquor's gypsum relative saturation was around 0.9. Thus, the increased oxidation rates observed in Phase II led to an increase of about 30 percent in the scrubber feed's gypsum relative saturation.

Although the oxidation rate increase did drive the scrubber feed liquor gypsum relative saturation upward, it did not cause supersaturated conditions in the reaction tank. Solids precipitated from such a liquor would not be expected to contain gypsum solids. An infrared scan of solids from 4-12-77 (Figure 4-1) supports this. The triplet peak in the 1100 to 1300 cm^{-1} range indicates that all of the solid phase sulfate exists in a solid solution with calcium sulfite. The formation of solid solution sulfate and subsaturated conditions in the precipitating liquor at sulfate/total sulfur ratios of less than 0.16 is supported by laboratory evidence (1).

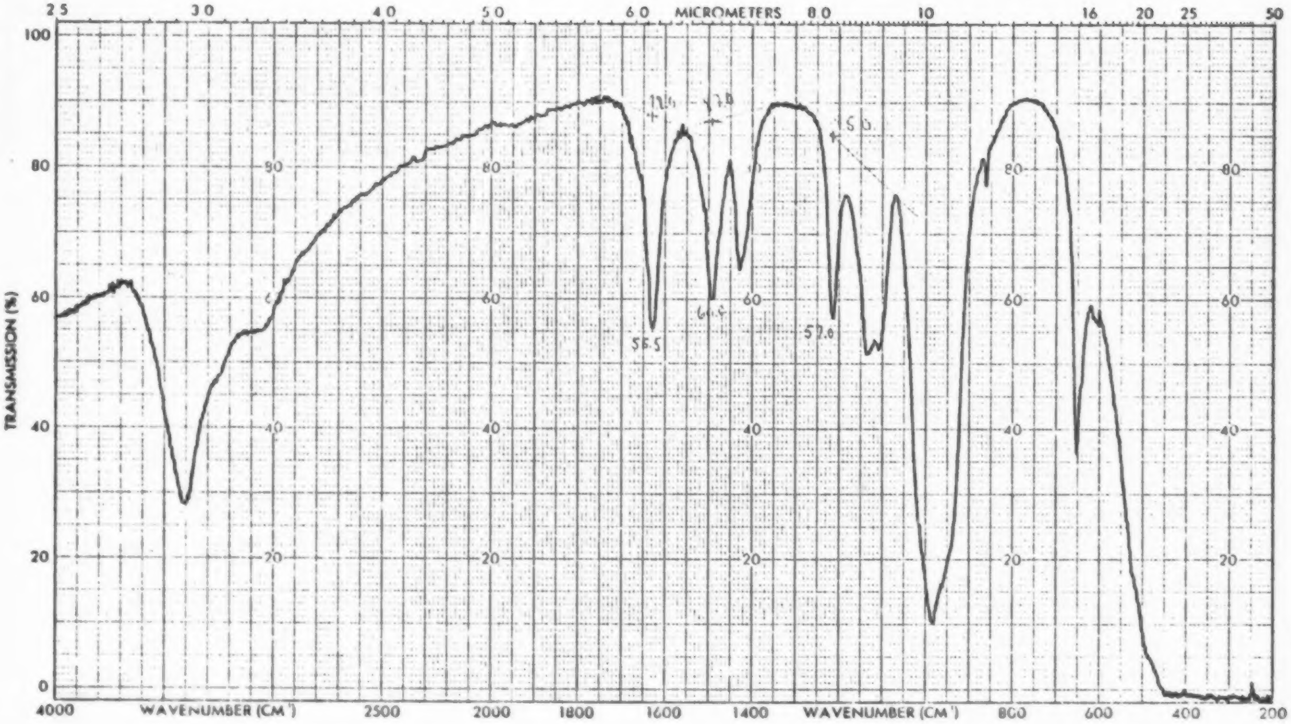


Figure 4-1. Infrared scan for Phase II solid sample taken 4-12-77.

Although the increased oxidation did not cause supersaturated conditions in the reaction tank, it did lead to gypsum scaling in the scrubber. As discussed above, the increased oxidation led to higher soluble sulfate levels and gypsum relative saturations in the scrubber feed This, in combination with calcium concentration increases due to solids dissolution, led to gypsum scaling conditions on the marble beds.

Examination of Table 3-3 shows that the gypsum relative saturation in the lower bed downcomer liquor was between 1.25 and 1.3. While a relative saturation of 1.3 to 1.4 is generally recognized as that required for the onset of gypsum scaling (2), it is noted that the lower bed downcomer sample was an average or composite sample of the lower bed liquor. As such, the lower bed downcomer sample does not provide information about specific sites on the bed. It appeared from scrubber inspections that the scaling was initiated in localized areas on the marble beds where the critical supersaturation was exceeded. Once gypsum scaling had started, crystal growth on the existing scale deposits soon resulted in extensive coverage of the marble beds by gypsum solids.

The major cause of the increase in gypsum relative saturation in the scrubber was from the increase in calcium concentration. Table 3-3 indicates that the gypsum relative saturation increased by 30 to 40 percent across the lower bed. Table 3-3 also shows that the calcium concentration increased about 50 percent across the lower bed while the sulfate concentration increased about 20 percent. Thus, calcium solids dissolution was the major contributor to the increase in gypsum relative saturation.

Although the calcium solids dissolution caused the relatively large increase in gypsum relative saturation, the scaling cannot be blamed on calcium dissolution alone. The percentage increases in calcium and sulfate concentrations and gypsum relative saturations noted during Phase I were similar to those measured in Phase II. However, since the gypsum relative saturation in the scrubber feed liquor was lower due to a lower oxidation rate in Phase I, the increase in relative saturation did not result in scaling conditions. In fact, the marble bed liquors were generally subsaturated with respect to gypsum in Phase I. Therefore, it was the combination of increased oxidation during Phase II and the calcium solids dissolution on the marble beds which led to the scaling conditions during commercial lime operation.

The increase in liquid phase calcium concentration in the scrubber was due to solids dissolution. This dissolution was caused by a deficiency in the liquid phase alkalinity present in the liquor on the marble beds. As SO_2 is sorbed, liquid phase alkalinity is consumed and driving forces are created for the dissolution of calcium carbonate and calcium sulfite solids which are alkaline with respect to the sorption of SO_2.

Referrring again to the infrared scan in Figure 4-1, it can be determined that calcium carbonate exists only as a solid solution with calcium sulfite and calcium sulfate. Therefore, the alkaline solid which must dissolve is the calcium sulfite-sulfate-carbonate solid solution. This conclusion is supported by the material balance results (see Material Balance Section).

From the preceding discussions, it is obvious that a significant reduction in calcium solids dissolution would help alleviate the scaling conditions. In theory, this could be done by significantly increasing L/G or by reducing the liquid retention time on the marble bed (which would effectively lower the removal). In practice, neither of these options was feasible.

It can be concluded from Phase II operation that commercial lime operation (with no other chemical additive) at Paddy's Run was impractical for two reasons: 1) inherently higher oxidation rates than those encountered with carbide lime operation, and 2) mechanical constraints which make operation at higher L/G's infeasible.

4.2 Effect of L/G and Slurry Solids Concentration Changes

Two operational changes were made in an attempt to reduce the scaling which was observed. The recirculating solids concentration and the scrubber feed rate were both increased. Neither change affected scrubber operation significantly, as explained below.

An increase in the slurry solids concentration was made to increase the seed crystal area available for crystal growth. An increase in crystal area should allow the required precipitation to occur at lower relative saturations. However, during Phase II, an increase in the slurry solids content did not increase the gypsum surface area available for precipitation because no gypsum solids were present in the recirculating scrubber liquor. As indicated in Figure 4-1, all of the solid phase sulfate was present in a solid solution with calcium sulfite. Therefore, the increase in solids concentration had little effect on the scaling potential in the scrubber. (Analytical results such as the I.R. analyses were not available prior to the decision to increase the slurry solids content.)

An increase in the scrubber feed rate should reduce the pickup per pass of SO_2 in the scrubber which should, in turn, help reduce the scaling rate. However, in this case, an increase in feed rate did not show a significant effect on the scaling rate. The feed rate was increased from 22,700 to 26,500 liters/min (6000 to 7000 gpm) on 3-17-77. Due to mechanical constraints, this higher feed rate was the maximum feasible for the Paddy's Run system. The liquid rate was increased in an effort to reduce the increase in liquid calcium and sulfate concentrations across the scrubber. However, it appears as if fluctuations in other variables such as inlet SO_2 concentration, gas flow rate, and SO_2 removal efficiency may have offset the 15 percent increase in scrubber feed flow. Little data was gathered prior to the increase so no definite trend twoard decreasing scaling potential was discernible with the increase in feed rate.

4.3 Material Balances

Data gathered on 4-12-77 was sufficiently complete to allow material balance calculations to be made. The results of these balances are summarized in Table 4-1. The calculational methods for these material balances are presented in Appendix F.

In considering these balances, some consistency checks should be made. An SO_2 pickup rate of 252 gmole/min was computed from gas data. The increase in liquid phase sulfur due to absorption was 265 gmole/min. Furthermore, the disposal rate of sulfur solids was 232 gmole/min. In theory, if the system was operating at steady-state, these three rates should be equal. Allowing for uncertainties in flow rates and an inability to sample all streams simultaneously, these numbers agree quite well. Therefore, within engineering limits, reasonable confidence may be placed in the precipitation rates calculated from these data.

TABLE 4-1. MATERIAL BALANCE RESULTS
Date 4-12-77

SCRUBBER

Gas phase SO_2 depletion = 252 gmol/min
Total sulfur increase (sorption plus dissolution) = 553 gmol/min
Total calcium increase = 309 gmol/min
Sulfur sorption (liquid) = 265 gmol/min

TOTAL SYSTEM

Oxidation rate = 38 gmol/min
Ca add rate = 142 gmol/min*
Ca solids out = 249 gmol/min
S solids out = 232 gmol/min
Lime utilization = .93
Oxidation fraction = .163

PRECIPITATION RATES (gmol/min)

	Scrubber	Draft tube	Hold tank	Total
$CaSO_3$	-292	502	- 8	202
$CaSO_4$	- 8	63	- 5	50
Total sulfur	-300	565	-13	252

Note: Calculational methodology is presented in Appendix F

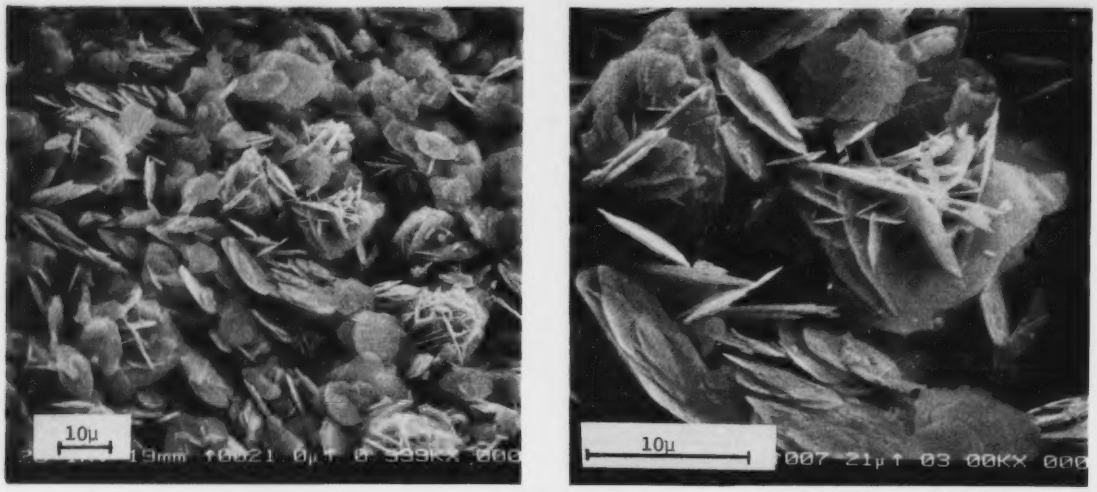
* Calibration of flow meter questionable.

Examination of the calculated precipitation rates listed in Table 4-1 reveals that calcium sulfite solids were dissolving in the scrubber. The significance of this was discussed in the previous section. It should also be noted that very little calcium sulfate dissolution or precipitation is calculated for the scrubber although gypsum solids were forming on the marble bed. The explanation for this is that the precipitation rate calculated is the net $CaSO_4$ precipitation rate. For each mole of calcium sulfite solids which dissolves, approximately 0.15 moles of calcium sulfate solids also must dissolve since the two exist as a solid solution. This may account for the negative net gypsum precipitation rate which was calculated even though gypsum solids precipitation was noted visually. Also, a scale deposition rate as small as 1 gmole per minute would result in 250 kg of gypsum being deposited in one day.

The precipitation rates in the draft tube are also important. It is obvious that most of the system's precipitation is occurring in the short residence time draft tube. This was also noted in Phase I.

4.4 Crystal Structure

Scanning electromicrographs for selected Phase II solids are presented in Figure 4-2. The solids at the conclusion of the phase (4-12-77) show a crystal structure similar to that seen in Phase I. The crystals here are basically rosettes. The solids from 3-21-77 (prior to the break for purging the interference from the system) are slightly different. There are still a significant number of rosettes present. However, there are also some platelets noted. These platelets are rounded, and the higher magnification shows that they are not single platelets but actually an aggregate platelet structure which has formed in layers.


10μ
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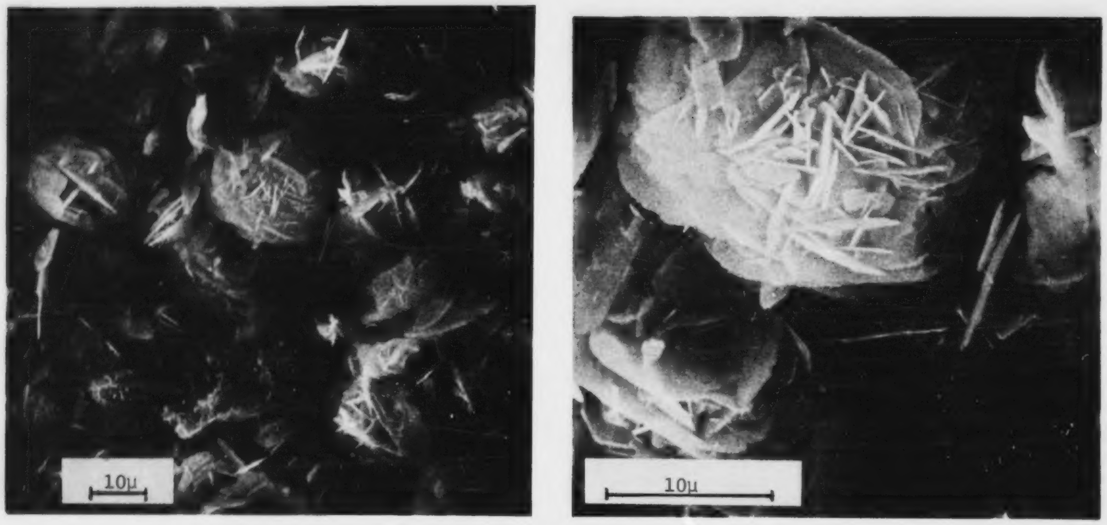
MARCH 21, 1977



APRIL 12, 1977

Figure 4-1. Electron micrographs for Phase II scrubber feed solids.

APPENDIX C

PHASE III
MAGNESIUM HYDROXIDE ADDITION

1.0 SUMMARY

Gypsum ($CaSO_4 \cdot 2H_2O$) scaling during the operation of the Paddy's Run system at base case conditions with commercial lime additive (Phase II) forced a redirection of the program. During a project review meeting held April 21, 1977, all of the project participants agreed that several changes in the original test program were warranted. First, magnesium addition was to be tested during a new Phase III in an attempt to make the Paddy's Run system operate successfully with commercial lime additive. Then, assuming the system could be made operable with magnesium spiking, hold tank modifications were to be tested in Phase IV, and the effect of chloride addition was to be studied in Phase V. Originally, the hold tank madifications tests were planned for Phase III, and the effects of both magnesium and chloride addition were to be studied in Phase IV.

The primary objective of the magnesium addition testing, which was performed in the revised Phase III, was to eliminate the scaling experienced during commercial lime operation. The addition of magnesium should increase the liquid phase alkalinity. This, in turn, should reduce the requirement for alkaline solids dissolution in the scrubber. Since the dissolution of calcium solids on the marble beds was a major cause of the scaling problems encountered during Phase II, it was believed that magnesium addition would help control the scaling. In theory, other process changes, such as an increase in scrubber L/G, could be used to accomplish the same result since any increase in available liquid phase alkalinity in the scrubber feed liquor should reduce the requirement for calcium solids dissolution. However, due to mechanical constraints, only limited increases in scrubber L/G at Paddy's Run were possible. Thus, magnesium addition was judged to be the most feasible solution to the scaling problem.

Magnesium addition was, in fact, instrumental in operating the Paddy's Run scrubber in a non-scaling mode with commercial lime. Several benefits were derived from the increased liquid phase alkalinity which was obtained at high magnesium levels. First, during Phase III, magnesium concentrations above 130 mmole/ℓ (3000 ppm) in the scrubbing liquor led to conditions which were subsaturated with respect to gypsum throughout the system. Another very significant effect of the high magnesium level was an increase in the SO_2 removal efficiency of the Paddy's Run scrubber (above 98 percent). At these conditions, negligible amounts of calcium solids dissolved on the marble beds. However, operation with magnesium concentrations below 95 mmole/ℓ (2300 ppm) resulted in significant calcium solids dissolution and scaling on the lower marble bed. The SO_2 removal efficiency at this magnesium level was 90 to 95 percent. The benefits of magnesium addition will vary depending upon several system specific factors such as mechanical design and coal composition. However, for the Paddy's Run system operating as it was during Phase III, the optimum soluble magnesium concentration was found to be in the 2500 to 3000 ppm range.

In addition to the direct effects of the increase in liquid phase alkalinity discussed above, increased magnesium levels led to a decrease in the sulfite oxidation fraction. The oxidation fraction varied between 0.08 and 0.12 when the magnesium concentration remained above 2500 ppm. An oxidation fraction of 0.19 was measured during the brief period in which the magnesium dropped into the 2000-2300 ppm range. During Phase II, when the magnesium concentration was less than 300 ppm, the oxidation fraction varied between 0.15 and 0.2. From these data, it appears that the magnesium concentration has some influence over the sulfite oxidation fraction obtained during operation with commercial lime. Some possible reasons for this effect are discussed in the results section of this appendix.

During the majority of the Phase III operating period Combustion Engineering (CE) was gathering data as part of an EPA sponsored sludge study. The CE work required that the system be operated at "steady-state" conditions for approximately six weeks. Liquid phase magnesium concentrations of greater than 3500 ppm were therefore maintained for most of this period and the normal flow configuration was employed as it had been for Phase I and II.

During Phase III, two potentially significant operating problems were noted. First, difficulty in controlling the slurry solids concentration was experienced for about one week. Second, "open loop" operation similar to that noted in Phase II, was found to be necessary to control system liquid levels. The causes of these problems and their influence on system operation are discussed in the following paragraphs.

A solids control problem which was first noted on July 12 lasted about one week. This problem was caused by poor solid-liquid separation in the clarifier which resulted from a change in the product solid characteristics.

The change in product solid crystal characteristics which was observed during this period appears to have been influenced by the increase in magnesium concentration which occurred during the same period. Increased magnesium concentrations should increase the soluble sulfur levels throughout the system. This, in turn, may promote increased nucleation in the draft tube which would tend to decrease the average size of the product sludge particles and increase the total number of particles. While this phenomenon could account for the observed behavior of the Paddy's Run clarifier, another problem complicates this interpretation. Unfortunately, the clarifier problems which were just discussed occurred during a period when the flocculant addition system was not functioning properly. Although a flocculant addition system malfunction would not be expected to cause the observed crystal structural change, it could have reduced the solid-liquid separation efficiency in the clarifier.

It is significant that no solid-liquid separation problems were noted in Phases I and II. Thus, solids settling problems encountered during Phase III may indicate that operation with magnesium addition may have an adverse impact on solids characteristics. However, the exact relationship between magnesium levels and sludge characteristics is probably very system specific.

The extent to which open loop operation was necessary during Phase III makes it difficult to accurately predict the effect of closed loop operation. While most of the same trends would be expected, it should be recognized that significant quantities of soluble magnesium and sulfur were being removed from the system during Phase III via the blowdown stream. If the liquor discharge rate were reduced, more solid sulfur precipitation would be required in the system, and potentially, magnesium levels higher than 130 mmoles per liter would have been required to keep the Paddy's Run system operable with commercial lime. In spite of these limitations, however, the trends shown in this phase (higher liquid phase alkalinities and lower sulfate/total sulfur ratios in the solid phase) should result from magnesium addition in any lime system.

The remainder of this appendix provides more specific details of the Phase III test results. Section 2.0 describes the test approach employed. A comprehensive summary of the Phase III test data is presented in Section 3.0. In Section 4.0, important results are discussed and the conclusions drawn from the Phase III test data are presented.

2.0 TEST APPROACH

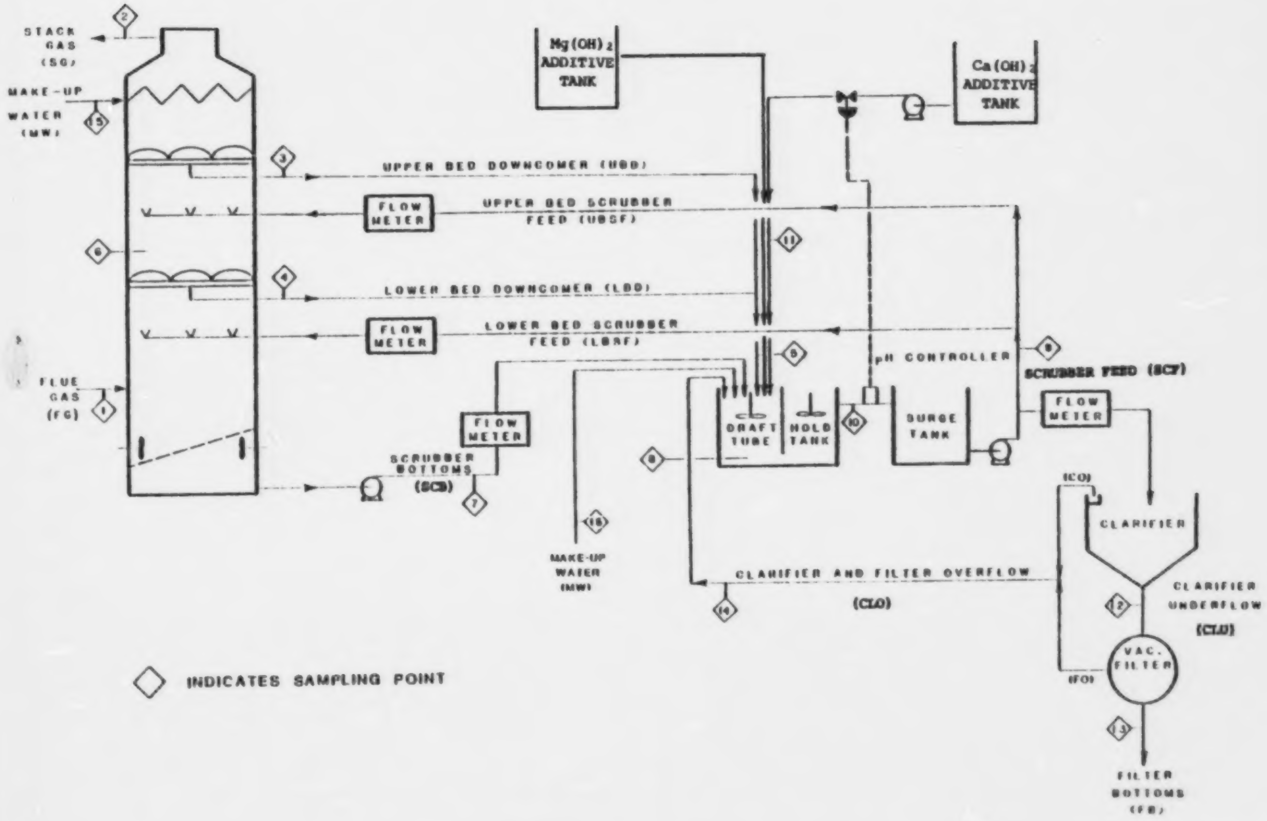
Phase III test objectives were reformulated on April 21, 1977, in a meeting attended by Radian, LG&E, C.E., and EPA representatives. Due to the unsuccessful scrubber operation observed with commercial lime during Phase II, a modified Phase III test program was developed. Specifically, magnesium spiking experiments were proposed to determine if high magnesium levels in the scrubbing liquor would lead to successful operation of the Paddy's Run system with commercial lime. The hold tank modification test work originally planned for Phase III was tentatively shifted to Phase IV. The planned chloride spiking tests were shifted to a new Phase V.

The reason for this revised test approach was the scaling exhibited during Phase II. As discussed in Appendix B, dissolution of calcium solids in the scrubber was a major factor which led to the scaling of the system's marble beds. Magnesium addition was the method selected for reducing the solid phase alkalinity requirement which caused the calcium dissolution on the beds. In theory, liquid phase alkalinity is enhanced by magnesium addition which therefore reduces the alkalinity required from the solid phase. Other possible solutions, such as a significant increase in scrubber L/G, were not feasible because of the mechanical limitations of the Paddy's Run system.

A conservative approach was adopted for Phase III testing. Initial work involved repairing damaged scrubber internals and adding a magnesium hydroxide storage tank. The scrubber was operated for four days in May with carbide lime to clean the gypsum scale from the marble beds. After this was done, the solids were allowed to settle in the hold tank. Then, the supernatant liquor was siphoned off to remove the interferring species present in the carbide lime scrubbing liquid. The process of reslurrying the solids, allowing the solids to settle, then siphoning the supernatant liquor was repeated three times.

Prior to Phase II start-up, the magnesium content of the liquor was increased by adding 19,000 liters of 50 percent $Mg(OH)_2$ slurry to the reaction tank. The system was then started up in the normal manner. The only deviation from the operating conditions employed during Phases I and II was the addition of the $Mg(OH)_2$ slurry to the draft tube. The process flow configuration used during Phase III is shown in Figure 2-1.

The rate of $Mg(OH)_2$ addition was set by the desired magnesium concentration in the scrubbing liquor. Chemical analyses were performed for soluble Mg^{++}, and the amount of $Mg(OH)_2$ addition was adjusted as necessary. The $Mg(OH)_2$ slurry was added in batches, typically four times per day.


STACK GAS (SG)
MAKE-UP WATER (MW)
FLUE GAS (FG)
Mg(OH)₂ ADDITIVE TANK
Ca(OH)₂ ADDITIVE TANK
UPPER BED DOWNCOMER (UBD)
FLOW METER
UPPER BED SCRUBBER FEED (UBSF)
LOWER BED DOWNCOMER (LBD)
FLOW METER
LOWER BED SCRUBBER FEED (LBRF)
pH CONTROLLER
SCRUBBER FEED (SCF)
FLOW METER
DRAFT TUBE
HOLD TANK
SURGE TANK
FLOW METER
SCRUBBER BOTTOMS (SCB)
MAKE-UP WATER (MW)
(CO)
CLARIFIER
CLARIFIER UNDERFLOW (CLU)
CLARIFIER AND FILTER OVERFLOW (CLO)
VAC. FILTER
(FO)
FILTER BOTTOMS (FB)
INDICATES SAMPLING POINT
1
2
3
4
5
6
7
8
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11
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14
15
16

Figure 2-1. Phase III process flow diagram.

3.0 RESULTS

A graphical summary of the process and analytical results obtained during Phase III is presented in Figure 3-1. These results are discussed in the subsections which follow. Section 3.1 describes the process results, and Section 3.2 presents the analytical data. Problems encountered during operation and discrepancies in the data are explained where necessary.

3.1 Process Data

Table 3-1 summarizes the process data gathered during Phase III. Basically, the same scrubber feed rate, pH, and recirculating solids concentration employed in Phase II were used in Phase III. However, some differences -n measured L/G's and solids contents between Phase II and III are apparent. During Phase III, the L/G fluctuated between 7.5 and 10.5 ℓ/Nm^3 due to differences in the gas flow rate. Although the boiler load was generally maintained at 35 MW, differences in operation, including a change in scrubber modules on July 19, led to the gas flow differences. During Phase II, the L/G had remained between 7.7 and 9.0.

Table 3-1 shows that the solids content was about 4.5 percent during the initial stages of Phase III compared to 6 - 7 percent during Phase II. This was not a result of an intentional change in the percent solid set point. This difference resulted from the density measurement method for slurry solids employed by LG&E. The higher TDS liquor which resulted from the magnesium addition made the slurry more dense for a given solids concentration and, in effect, lowered the solids set point.

TABLE 3-1. PHASE III - PROCESS MEASUREMENTS

Test Objective: Determine the Effect of Magnesium Addition on System Operation.

	Test #14								
	June 19	June 22	June 27	July 6	July 8	July 18	July 21	July 22	July 25
Flue gas (Nm^3/hr) (dry)	-	196,000	203,000	196,000	207,000	212,000	151,000	167,000	169,000
SO_2 inlet (ppm)	-	2,160	2,160	2,150	2,060	1,800	2,240	2,090	3,040
SO_2 outlet (ppm)	25	10	-	10	10	20	5	7	13
Removal efficiency (%)	-	99	-	$99.^+$	$99.^+$	99.	$99.^+$	$99.^+$	99.
Scrubber feed (ℓpm)	26,500	→	→	26,900	→	26,500	→	→	→
Upper bed	13,300	→	→	13,500	→	13,300	→	→	→
Lower bed	13,200	→	→	13,400	→	13,200	→	→	→
L/G (ℓ/Nm^3)		8.1	7.8	8.2	7.8	7.5	10.5	9.5	9.4
Scrubber feed pH	8.0	7.8	8.0	7.9	7.9	7.6	8.3	8.2	8.0
Recirculating slurry solid concentration (%wt.)	4.9	4.5	4.7	4.0	4.4	8.4	5.8	5.6	6.2
Scrubber bottoms (ℓpm)				4,160	4,160		4,160	4,350	4,770
Clarifier feed (ℓpm)		760	660	760	750	760	750	760	760
Clarifier overflow (ℓpm)				712					
Filter bottoms (kg/min)			101	126					
Lime additive (ℓpm)	220	228	195	180	165		205	205	290
Makeup water (ℓpm)				190					

Note: The downcomer flow rates may be estimated as follows. The reject from each bed is assumed to be equal to the scrubber bottoms flow rate and approximately 190 liters/minute is assumed to be evaporated from the lower bed feed liquor.

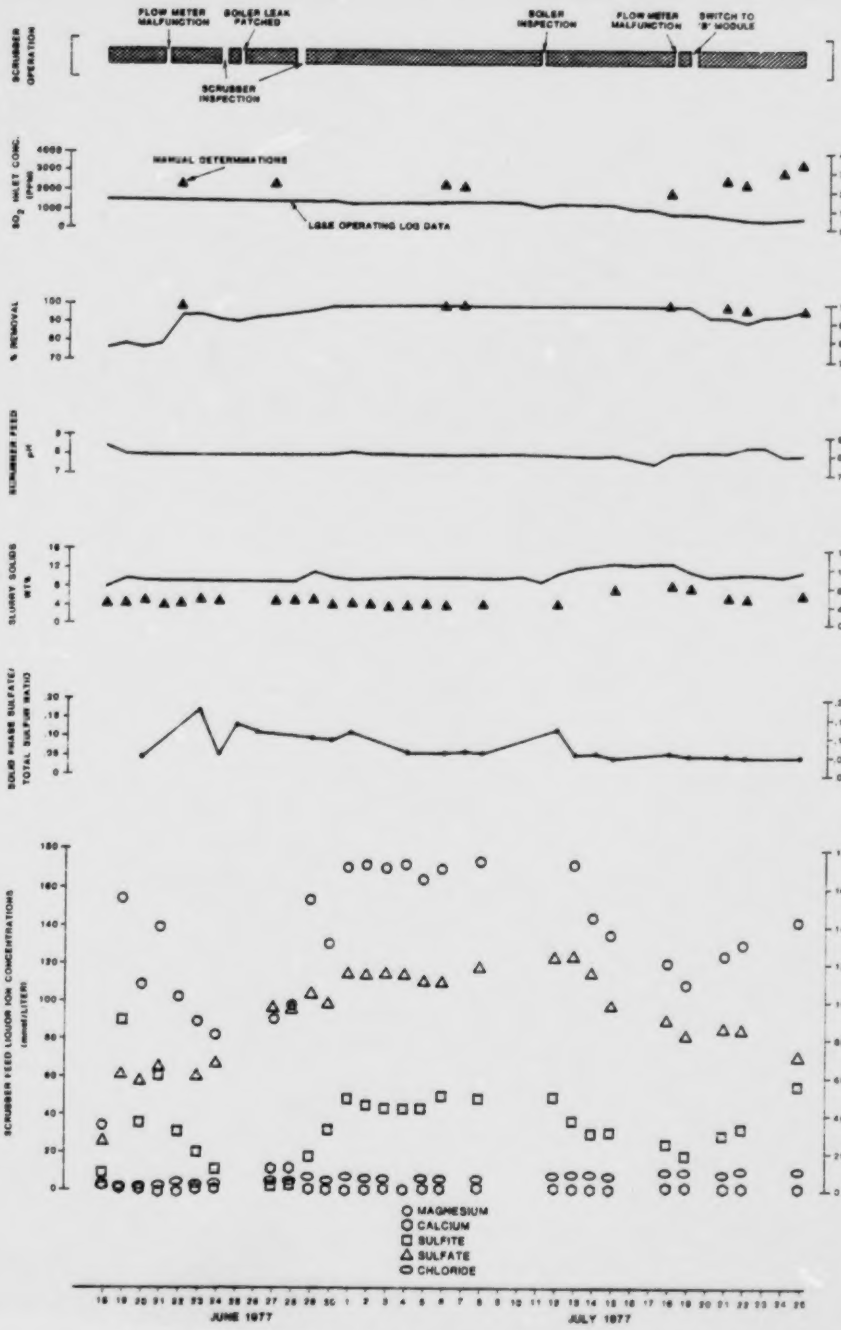

Figure 3-1. Summary of Phase III process and analytical results.

Phase III System operation began on June 18 with the start-up of Module A. Inspection of Figure 3-1 shows that scrubber operation was interrupted six times during Phase III. Brief outages were experienced on June 21, 24, and 28. Additional down time occurred on July 11, 18, and 19.

The June outages resulted from a flow meter malfunction and two scrubber inspections. The flow meter problem occurred on June 21. Only a brief period of time was required for the necessary repairs. Scrubber inspections were made on June 24 and 28. The first inspection indicated that subsaturated operation had been achieved since the remaining scale from Phase II had been dissolved from the beds. However, the inspection on 6-28 revealed that substantial amounts of scale had been redeposited on the lower bed. This scale build-up was associated with the reduction in liquid phase magnesium concentrations which occurred in late June. Tighter control over the magnesium addition rate was instituted, and the magnesium concentration was maintained above 130 mmoles/liter (3000 ppm) for most of the remainder of Phase III.

In July, system operation was stopped on three occasions. None of these outages were a result of process chemistry problems. A brief boiler inspection for possible tube leaks was made on July 11. The leaks were not serious enough to force shutdown for tube repair. The outages experienced on July 18 and 19 were associated with a malfunction of the flow meter in the lower bed feed line. Due to the time and expense involved in repairing this flow meter, Module B was placed in service. No further down time occurred through July 25, the conclusion of Phase III.

Throughout Phase III, the SO_2 removal efficiency remained above 90 percent. The inlet SO_2 concentrations were generally in the 2000-2500 ppm range as determined by manual sampling and analysis. The average SO_2 outlet concentration was less than 100 ppm.

As was the case throughout the program, the DuPont readings were consistently lower than the manual determinations. However, beginning about mid-July, the DuPont measurements indicated a decline in the inlet gas SO_2 content. As can be seen in Figure 3-1 this decrease in SO_2 was not supported by manual analysis. After the completion of Phase III, a leak was discovered in the sample line from the inlet gas stream to the DuPont analyzer. This problem was corrected during Phase IV. As a result of this leak, the DuPont results for the latter half of July are probably not indicative of actual operating conditions.

Figure 3-1 also indicated that the outlet DuPont measurements were high during the initial stages of Phase III. This problem was traced to the location of the DuPont sample ports in the outlet gas duct. The sample port was located just upstream of the junction of the ducts from the two scrubber modules. Flue gas leaking though the damper system of the non-operating scrubber module, together with eddy currents, probably allowed some of this unscrubbed gas to reach the sample port for the operating scrubber module. High outlet SO_2 readings resulted. This problem was handled by opening several access ports in the non-operating module. When this was done, air leakage replaced flue gas leakage, and lower DuPont measurements were recorded. Since Radian's manual samples were taken from a sampling port well upstream of the DuPont sampling tap, sample dilution should not have been a problem.

Although the erroneous DuPont readings caused some initial data interpretation problems, they actually did not affect the system operation. However, there were two deviations from normal conditions which did significantly influence system operation. These were 1) a liquor level control problem which resulted in open loop operation and 2) an inability to control the recirculating slurry solids concentration.

The need for open loop operation was caused by a problem similar to that encountered during Phase II. The commercial lime slurry solids concentration typically ranged between 12 and 14 percent (compared to the 20-25 percent design range for carbide lime). The excess liquor entering with the lime solids had to be purged by bleeding an average of 75 liters/min of clarifier overflow from the system. During Phase III, this blowdown liquor contained significant amounts of both magnesium and soluble sulfur species.

A problem in controlling the recirculating slurry solids content was also observed during Phase III. Although the lack of solids control did not necessitate system shutdown, the problem was significant. A "cloudy" clarifier overflow stream was noticed by operating personnel on July 12. This overflow stream contained 5.7 percent solids on July 14. Typically, this stream contained less than 0.1 percent solids. As a result of the increased solids in the overflow, the solids level in the recirculating scrubbing liquor rose from about 4 percent to between 7 and 10 percent during the period of July 12 to July 19. On the nineteenth, negligible solids were observed in the clarifier overflow, and the solids level in the scrubber feed stream began to decline. Control of the slurry solids content at the desired lower value was reestablished by July 21.

3.2 Analytical Data

Table 3-2 presents the detailed chemical analyses results obtained during Phase III. As can be seen from this table, initial magnesium concentrations of 130 to 160 mmoles per liter were established. Since the oxidation fraction computed from solids analyses was less than 0.05 and the gypsum relative saturation in the scrubbing liquor was less than 0.1, the magnesium concentration was lowered. However, as the magnesium level dropped to between 80 and 90 mmole/liter, the oxidation fraction rose. On June 27 and 28, the solid phase sulfate/total sulfur ratios were 0.13 and 0.12 respectively and the gypsum relative saturation approached 0.9 in the scrubber feed and 1.5 on the lower bed. Scaling was visually confirmed on June 28.

Following a brief scaling period, the magnesium level was increased and then maintained between 130 and 180 mmoles per liter for the remainder of Phase III. During this period, the oxidation fraction was generally in the 0.05 to 0.1 range and the system remained subsaturated with respect to gypsum (gypsum relative saturations below 0.1 were common).

The liquid phase calcium values were lower during Phase III than in either of the first two phases, but more importantly, the increase in calcium concentration across the scrubber remained quite low except for the period when scaling was noted.

TABLE 3-2. CHEMICAL DATA SUMMARY

Sample identification			Slurry properties			Liquid analyses (mmole/liter)							Solid analyses (mmol/g)						Computer results		
Date	Stream^1	Time	pH	Temp (°C)	% Solids	Ca^{++}	Mg^{++}	Na^+	Cl^-	$CO_3^=$	$SO_3^=$	$SO_4^=$	Ca^{++}	Mg^{++}	$CO_3^=$	$S.SO_4^=$	T.S.	Ox Frac	$CaSO_3$,RS	$CaSO_4$,RS	P^*SO_2(PPM)^2
6-18	SCF	11:40	8.7	42	4.6	2.90	34.8	1.19	1.96	-	9.21	25.0							4.32	.10	.00001
	LBD	-	8.2	48		1.45	55.8	3.17	1.94	-	21.3	32.6							3.05	.04	.0002
6-19	SCF	-	8.0	49	4.9	<1.0	155.	7.04	3.08	-	90.4	61.4							3.11	.02	.002
	LBD	-	7.0	51		<1.0	163.	8.26	3.99	-	99.5	54.5							2.89	.02	.18
6-20	SCF	-	8.0	50	5.4	.95	108.	7.35	3.60	-	36.1	57.4	7.52	.05	-	.30	6.45	.047	2.28	.03	.0009
	LBD	-	7.0	52		1.17	127.	6.10	5.18	-	48.8	63.3							2.36	.03	.11
6-21	SCF	14:10	7.9	49	4.2	.86	139.	9.20	3.78	-	61.9	65.4							2.41	.02	.002
	LBD	14:20	6.9	51		.59	144.	10.1	3.92	-	72.2	67.5							2.66	.03	.21
6-22	SCF	-	7.8	49	4.5	1.30	110.	3.25	4.33	6.4	30.7	68.5	-	-	.97				2.53	.05	.001
	LBD	-	6.3	51		1.53	103.	3.81	4.33	6.2	42.9	68.0							2.16	.06	1.3
6-23	SCF	10:30	8.0	49	5.4	1.35	87.9	-	3.42	5.0	19.8	60.5	-	-	-	-	6.80	.169	2.08	.06	.0005
	LBD	11:00	6.1	52		3.26	91.8	-	3.66	3.4	35.0	64.0							3.39	.14	2.3
	UBD	10:45	6.9	51		1.64	87.1	-	3.31	7.2	21.7	61.9							2.25	.07	.073
6-24	SCF	13:40	8.0	49	4.9	2.42	83.6	2.47	3.93	2.2	11.6	67.5	7.28	.15	.446	.39	6.70	.059	2.45	.13	.0003
	LBD	14:00	6.1	52		6.12	86.8	2.55	4.10	1.8	27.9	68.0							3.49	.32	4.5
	UBD	13:50	6.9	51		3.58	84.8	2.51	4.03	4.1	17.2	67.1							2.98	.19	.39
6-27	SCF	13:45	8.0	49	4.7	12.6	91.1	-	4.62	-	3.40	96.3	7.32	.00	.40	.89	6.77	.131	3.07	.89	.00006
	LBD	14:10	5.2	51		23.0	91.6	-	4.68	-	21.5	95.9							2.96	1.47	14.
6-28	SCF	9:00	8.1	51	5.0	12.8	96.5	-	4.93	1.8	3.47	95.8	7.28	.06	.45	.76	6.40	.119	3.05	.88	.00004
	LBD	9:25	5.2	55		23.2	98.4	-	4.94	2.4	22.1	101.							2.72	1.47	18.
	UBD	9:00	5.7	52		17.8	98.9	-	4.88	3.0	13.7	98.3							3.76	1.16	.08
6-29	SCF	9:15	8.0	49	5.1	2.39	124.	-	-	4.7	17.8	103.	7.62				7.14		-	-	-
	LBD	9:30	5.9	52		-	-	-	-	2.4	37.9	104.							-	-	-
	UBD	9:30	6.7	52		-	-	-	-	7.4	21.3	105.							-	-	-
	SCF	17:00	7.9	50	4.4	1.21	154.	-	7.04	7.7	42.4	103.				.637	6.71	.095	2.21	.05	.001
	LBD	17:10	6.4	52		1.66	156.	-	5.79	1.7	56.0	109.							2.44	.07	1.1
6-30	SCF	10:00	7.8	50	4.6	1.40	130.	-	5.47	8.5	33.3	99.3	-	-	-	.61	6.72	.091	2.37	.06	.002
	LBD	10:00	6.5	52	-	2.40	140.	-	5.91	5.4	50.7	102.							3.70	.11	.73
	UBD	10:00	7.2	52	-	1.74	141.	-	5.55	11.7	35.2	101.							2.68	.08	.027
	CLO	10:00	7.3	45	-	1.57	142.	-	5.19	4.2	28.0	107.							-	-	-
7-1	SCF	9:10	8.2	50	4.1	.35	171.	-	8.27	12.2	48.1	114.	7.06	.04	.52	.80	7.05	.113	.65	.01	.0003
	LBD	9:10	6.8	52		.6	168.	-	-	8.1	62.4	115.							-	-	-
	UBD	9:10	7.4	51		.1	167.	-	-	24.0	47.8	108.							-	-	-
	CLO	9:10	6.6	45		.1	167.	-	-	9.0	40.3	118.							-	-	-
7-2	SCF	9:30	8.0	48	4.1	1.22	173.	-	6.37	7.8	45.1	117.	-	-	.75	-	-	-	2.22	.05	.0007
	LBD	9:40	6.5	51		1.0	171.	-	-	10.6	59.7	114.							1.60	.04	.73
	UBD	9:50	7.1	51		1.51	173.	-	-	18.6	43.9	117.							2.40	.07	.043
	CLO	9:30	7.9^2	45		1.38	168.	-	-	8.8	43.7	114.							2.57	.06	.0009
7-3	SCF	9:10	7.9	49	3.8	1.47	170.	-	6.40	10.0	43.7	115.							2.61	.06	.001
	LBD	9:20	6.5	51		-	-	-	-	8.0	60.3	107.							-	-	-
7-4	SCF	11:00	8.0	49	4.0	1.29	173.	-	-	11.1	42.8	115.	-	-	.52	.38	6.55	.058	2.24	.06	.0007
	LBD	11:00	6.5	51		1.72	174.	-	-	10.5	56.0	119.							2.58	.08	.67

(Continued)

TABLE 3-2. CHEMICAL DATA SUMMARY (Continued)

Sample identification			Slurry properties			Liquid analyses (mmol/liter)							Solid analyses (mmole/g)						Computer results		
Date	Stream¹	Time	pH	Temp (°C)	% Solids	Ca^{++}	Mg^{++}	Na^+	Cl^-	$CO_3^=$	$SO_3^=$	$SO_4^=$	Ca^{++}	Mg^{++}	$CO_3^=$	$S.SO_4^=$	T.S.	Ox Frac	$CaSO_3RS$	$CaSO_4RS$	P^*SO_2(PPM)²
7-5	SCF	8:30	8.0	50	4.2	1.36	165.	-	6.47	11.4	43.4	110.							2.44	.06	.0008
	LBD	8:40	6.7	53		1.49	166.	-	-	9.3	56.7	110.							2.53	.06	.31
	UBD	8:50	7.3	52		1.33	164.	-	-	14.0	45.6	110.							2.31	.06	.019
7-6	SCF	9:30	7.9	51	4.0	1.26	170.	4.00	6.51	10.9	49.8	110.	7.32	.15	.40	.37	6.58	.056	2.52	.05	.002
	LBD	9:15	6.5	53	-	1.50	173.	-	-	9.2	63.3	113.							2.34	.06	1.0
	UBD	9:15	7.1	53	-	1.24	169.	-	-	20.3	49.3	113.							2.09	.05	.054
	DTE	9:45	7.7	50	-	1.71	171.	-	-	12.7	48.1	111.							3.17	.07	.003
	SCB	9:45	6.1	52	-	1.77	176.	-	-	6.63	77.1	108.							2.42	.07	3.8
	CLU	10:00	8.7	35	21.0	1.30	156.	3.40	-	8.7	38.9	106.	7.56	.12	-	.46	6.80	.068	2.62	.06	.00001
	CLO	10:00	7.9	40	-	1.21	163.	-	-	8.8	41.1	114.							2.17	.05	.0009
	LA	10:00	12.3	25	12.3	7.21	.0	-	-	.0	.0	-	12.6	-					-	-	-
	MgA	10:00	10.3	25	57.3	0.0	10.7	-	-	-	.0	-		16.9					-	-	-
	MW	10:00	7.5	30	-	1.19	.38	-	1.09	2.1	.0	.95							-	-	-
	FB	10:00	-	-	36.6	-	-	-	-	-	-	-							-	-	-
7-8	SCF	8:20	7.9	50	4.4	1.52	174.	2.91	6.8	14.7	47.1	117.	7.12	.25	.65	.35	6.55	.056	2.78	.07	.001
	LBD	8:10	6.7	53	-	1.59	180.	-	-	9.55	58.9	120.							2.65	.07	.35
	UBD	8:10	7.2	53	-	1.40	173.	-	-	24.0	49.3	114.							2.46	.06	.039
	SCB	8:35	6.3	53	-	1.89	172.	-	-	8.5	72.6	117.							2.90	.08	2.0
	DTE	8:45	7.6	48	-	1.71	172.	-	-	14.7	47.7	116.							3.19	.07	.005
	CLO	8:30	8.2	30	-	1.41	175.	-	-	14.0	41.5	122.							2.85	.07	.0001
	CLU	8:30	8.6	30	18.7	1.40	162.	-	-	11.7	37.9	113.	7.37	-	.71	.49	6.69	.073	2.80	.07	.00001
	LA	8:30	12.4	25	13.2	-	-	-	-	-	-	-			1.14				-	-	-
	MgA	8:30	10.3	25	54.1	-	-	-	-	-	-	-			.25				-	-	-
7-12	SCF	8:30	7.9	50	-	<1.0	184.	-	7.65	-	48.0	123.	7.00	.31	.31	.83	6.69	.124	-	-	-
	LBD	8:40	6.7	53	-	<1.0	185.	-	-	-	62.5	122.							-	-	-
	UBD	8:50	7.3	52	-	<1.0	186.	-	-	14.4	48.9	125.							-	-	-
7-13	SCF	8:30	7.9	51	9.6	1.45	173.	-	8.2	7.95	36.4	125.	7.55	.12	.40	.37	6.74	.055	2.15	.07	.001
	LBD	8:40	6.3	55	-	2.06	175.	-	-	5.08	53.6	124.							2.43	.10	1.6
	SCB	8:50	5.8	53	-	2.41	171.	-	-	4.06	64.2	128.							1.86	.12	9.1
7-14	SCF	7:40	7.5	50	-	1.48	145.	-	8.27	5.93	30.3	115.	7.64	.33	-	.42	6.90	.061	2.10	.08	.005
	LBD	7:55	6.2	53	-	2.49	154.	-	-	3.77	47.7	109.							2.70	.12	1.7
	SCB	8:10	5.9	51	-	3.08	147.	-	-	3.21	53.9	116.							2.64	.16	5.5
	CLO				5.7																
7-15	SCF	7:40	8.3	50	7.8	1.44	135.	-	7.26	-	31.7	95.8	7.49	.05	-	.30	6.68	.045	2.37	.07	.002
	LBD	8:05	6.3	53	-	2.13	136.	-	-	-	45.3	97.5							2.62	.10	1.4
	SCB	7:55	6.0	50	-	2.51	140.	-	-	-	54.7	105.							2.61	.12	4.0
	CLO				4.2																
7-18	SCF	8:15	7.6	50	8.4	1.54	120.	-	9.9	-	25.3	88.2	7.26	.05	-	.43	6.75	.064	2.16	.07	.003
	LBD	8:20	6.0	55	-	2.47	113.	-	-	-	43.0	79.6							2.31	.11	4.1
	SCB	8:30	5.7	52	-	3.35	123.	-	-	-	48.1	90.5							2.17	.17	9.6
	CLO	-	-	-	5.7	-	-	-	-	-	-	-	7.00	-	.55	-	-	-	-	-	-
7-19	SCF	8:20	8.3	47	7.6	1.7	108.	-	9.6	-	18.6	81.7	7.31	.20	-	.33	6.46	.051	2.19	.09	.00009
	LBD	8:40	5.3	55		11.1	115.	-	-	-	54.6	89.9							3.56	.55	36.
	SCB	8:30	5.3	50		4.0	107.	-	-	-	39.5	85.8							1.15	.22	22.

(Continued)

TABLE 3-2. CHEMICAL DATA SUMMARY (Continued)

Sample identification			Slurry properties			Liquid analyses (mmol/liter)							Solid analyses (mmol/g)						Computer results		
Date	Stream[1]	Time	pH	Temp (°C)	% Solids	Ca^{++}	Mg^{++}	Na^{+}	Cl^{-}	$CO_3^{=}$	$SO_3^{=}$	$SO_4^{=}$	Ca^{++}	Mg^{++}	$CO_3^{=}$	$S.SO_4^{=}$	T.S.	Ox Frac	$CaSO_3$RS	$CaSO_4$RS	$P*SO_2$(PPM)
7-21	SCF	8:25	8.3	50	5.8	1.51	124.	-	8.35	-	28.9	83.8	7.31	.27	.73	.31	6.28	.049	2.44	.0.	.0001
	LBD	8:55	6.6	52	-	2.02	124.	-	-	-	41.9	83.4							3.14	.08	.42
	UBD	9:15	7.2	52	-	2.43	120.	-	-	-	33.6	77.8							4.07	.10	.028
	SCB	8:40	6.4	50	-	1.87	131.	-	-	-	51.0	84.9							2.92	.07	.98
7-22	SCF	8:35	8.2	50	5.6	1.36	130.	-	10.4	-	33.6	83.6	7.49	.03	-	.28	6.28	.045	2.39	.06	.0003
	LBD	9:15	6.7	52	-	1.52	133.	-	-	-	43.5	87.5							2.47	.06	.29
	UBD	9:05	7.0	52	-	1.56	131.	-	-	-	34.6	87.8							2.41	.07	.064
	SCB	8:45	6.3	51	-	1.32	142.	-	-	-	55.4	89.8							1.92	.05	1.5
7-25	SCF	8:55	8.0	50	6.2	.93	142.	2.10	10.5	7.67	56.7	69.9	7.70	.00	.53	.33	6.67	.049	2.27	.03	.001
	LBD	9:30	6.6	53	-	.86	151.	-	22.0	-	69.0	77.5							1.73	.03	.61
	UBD	9:20	7.2	52	-	.83	141.	-	12.2	-	55.9	71.9							1.85	.03	.041
	SCB	9:05	6.0	51	-	1.50	145.	-	31.5	-	86.9	84.6							2.15	.05	6.8
	DTE	9:40	8.1	47	-	1.56	131.	-	20.6	-	46.8	72.4							3.64	.05	.0006
	CLO	9:30	7.7	30	-	1.03	132.	-	17.5	-	41.5	81.4							2.45	.04	.003
	CLU	9:30	8.7	30	26.3	1.02	131.	2.03	18.6	4.30	39.2	81.0	7.76	.00	.53	.37	6.52	.057	2.4	.04	.00003
	LA	9:40	12.1	25	12.0	14.8	-	-	1.43	-	1.07	.11	12.9	-					-	-	-
	MgA	9:30	10.5	20	53.3	-	26.3	-	71.5	-	.19	.95	-	15.9					-	-	-
	MW	9:30	8.3	25	-	1.34	.50	-	1.03	-	.24	.99							-	-	-

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[1] Stream Identification
SCF - Scrubber Feed
LBD - Lower Bed Downcomer
UBD - Upper Bed Downcomer
SCB - Scrubber Bottoms
DTE - Draft Tube Effluent
CLO - Clarifier Overflow
CLU - Clarifier Underflow
LA - Lime Additive
MgA - Magnesium Additive
FB - Filter Cake Bottoms
MW - Makeup Water

4.0 DISCUSSION OF RESULTS

The objective of Phase III testing was to determine the effect of magnesium addition on the operability of the Paddy's Run system. During Phase II, the system could not be operated with commercial lime as the only additive due to significant gypsum scaling problems. However, the system was operated successfully with commercial lime additive supplemented by magnesium hydroxide addition. This section discusses the implications of important Phase III operating results and problems.

4.1 Operating Results

Operation with magnesium addition during Phase III is highlighted by two important process chemistry effects. First, as expected, an increase in liquid phase alkalinity resulted from increased soluble magnesium concentrations. Second, and perhaps more important, magnesium addition was demonstrated to be a viable means of reducing the scaling potential of the Paddy's Run scrubbing liquor. These effects are described in the following paragraphs.

The effects of the increased liquid phase alkalinity can be documented by comparing SO_2 removal efficiency and calcium solids dissolution for Phase III with the same variables from Phase II. Figure 3-1 and Table 3-1 show that the SO_2 removal efficiency during Phase III was generally above 98 percent for SO_2 concentrations in the range of 1800 to 3000 ppm. For similar SO_2 loadings, the removal efficiencies in both Phases I and II were between 70 and 80 percent. This difference in SO_2 removal can be explained as follows.

Basically, magnesium salts such as $MgSO_3$, $MgCO_3$, $MgSO_4$, etc. are more soluble than the corresponding calcium salts. Thus, liquid phase alkalinity in a high magnesium system is enhanced by the presence of greater quantities of soluble salts such as $MgSO_3$ which are alkaline with respect to SO_2 sorption. To the extent that the alkalinity necessary to react with sorbed SO_2 is available in the liquid phase, solid phase alkalinity is not required. Since the dissolution rate of most solids is slow compared to typical liquid phase acid-base reactions, higher removal efficiencies are possible in a fixed system as the magnesium concentration increases.

In addition to the higher SO_2 removal measured, the effect of magnesium on liquid phase alkalinity is also indicated by the rate of calcium solids dissolution which were observed in the scrubber during Phase III. This reduction in calcium solids dissolution can be seen by examining the calcium values shown in Table 3-2 and by studying the material balance summaries presented in Tables 4-1 and 4-2. From this information, it is seen that 1) the soluble calcium concentrations in Phase III (about 1 mmole/ℓ in the scrubber feed) were substantially lower than those observed during Phases I and II (15 to 20 mmole/ℓ in the scrubber feed) and 2) the calcium solids dissolution rate was negligible during most of Phase III. Thus, the theory that increasing the magnesium concentration leads to increases in liquid phase alkalinity is supported both by higher SO_2 removal efficiencies and the lower calcium solids dissolution rates which were observed.

As was mentioned previously, perhaps the most important result from Phase III was that magnesium addition allowed the system to operate in a scale-free manner. Certainly, the liquid phase alkalinity considerations discussed above have a major impact on system operability. During Phase II, the

TABLE 4-1. PHASE III MATERIAL BALANCE RESULTS (gmole/min)

Date	$\Delta SO_2(g)$	$\Delta S(liq)$	$\Delta Ca(liq)$	Sulfur sorption (liq)	Ca add rate	Ca solid out	Lime utilization	S Solid out	S liq[2] out	Total S out	Solid sulfate out	Liquid sulfate out	Oxidation rate	Oxidation fraction: sulfate/ total sulfur in solids	Oxidation fraction: sulfate/ total sulfur (solid+liquid)
6-27	-	-	-	-	-	236	.92	218	15	233	29	14	43	.131	.19
7-6	313	307	5	303	280	254	.89	227	24	251	13	17	30	.056	.12
7-8	315	269	1	268	280	244	.92	225	25	250	12	18	30	.056	.12
7-21	252	232	16	218	337	333	.86	286	17	303	14	13	27	.049	.089
7-22	260	327	3	324	337	330	.84	277	18	295	12	13	25	.045	.085
7-25	383	453	1	452	475	376	.87	326	18	344	16	11	27	.049	.078

[1] Lime utilization = S solid out/Ca solid out

[2] Estimate of 151 ℓpm used for liquid exit rate

Note: Calculational methodology is presented in Appendix F.

dissolution of calcium solids on the marble beds was identified as a major contributor to the gypsum scaling problems which were experienced. Magnesium concentrations above 125 mmole/liter supplied sufficient liquid phase alkalinity such that the rate of solids dissolution in the scrubber was minimized.

TABLE 4-2. CHEMICAL REACTION CALCULATION SUMMARY FOR 7-6-77

	Scrubber	Holding system		Total system
Reaction Rate (gmole/min)		Draft tube	Hold tank	
SO_2 Sorption	313	-	-	313
Oxidation	-	-	-	38
Calcium sulfite precipitation	-5	326	-46	275
Calcium sulfate precipitation	-1	12	27	38
Calcium carbonate precipitation	-	30	48	-
Calcium hydroxide dissolution	-	339	17	356

In addition to the reduction in solids dissolution in the scrubber, increased soluble magnesium concentrations resulted in a reduction in the sulfite oxidation fraction. For magnesium concentrations above 125 mmole/liter, the solid sulfate/total sulfur ratios were typically 0.04 to 0.09. However, since significant quantities of soluble sulfur were exiting in the liquor leaving the system, the overall oxidation fraction was between 0.08 and 0.12. This is reflected in the results shown in Table 4-1. The gypsum relative saturations were generally below 0.1. These values are lower than the 0.15 to 0.20 oxidation fractions and the 0.9 to 1.3 gypsum relative saturations measured during Phase II.

System operation with about 90 mmole/liter soluble magnesium concentrations deviated substantially from operation with higher magnesium levels. Between June 23 and 28, operation with 85-95 mmole/liter magnesium yielded oxidation fractions as high as 0.19 (0.13 in solid phase). Gypsum relative saturations above 1.4 on the lower bed were calculated for June 27 and 28, and scaling was noted visually on June 28. The soluble calcium values in the system increased from less than 1 to about 12 mmole/liter in the scrubber feed stream on these days, and significant calcium dissolution in the scrubber was calculated. The pH on the lower bed dropped from above 6 with greater than 125 mmoles per liter magnesium to 5.2 with about 95 mmole/liter magnesium on June 28. DuPont measurements indicated that the SO_2 removal efficiency dropped from 98 to 90-92 percent during this same time period. Overall, system chemistry with 90 mmoles per liter soluble magnesium closely paralleled that noted during Phase II with respect to oxidation, gypsum relative saturation, calcium dissolution, and scaling.

It appears that the decreases in liquid phase alkalinity which resulted from the decreases in magnesium concentration led to increased oxidation and gypsum scaling problems in the Paddy's Run system. The increase in oxidation observed with decreasing pH has been noted in other systems. When the magnesium concentration dropped below 100 mmole/liter, the increase in gypsum relative saturation in the scrubber feed liquor combined with the increase in calcium solids dissolution in the slurry on the marble beds led to gypsum scale build-up in the scrubber.

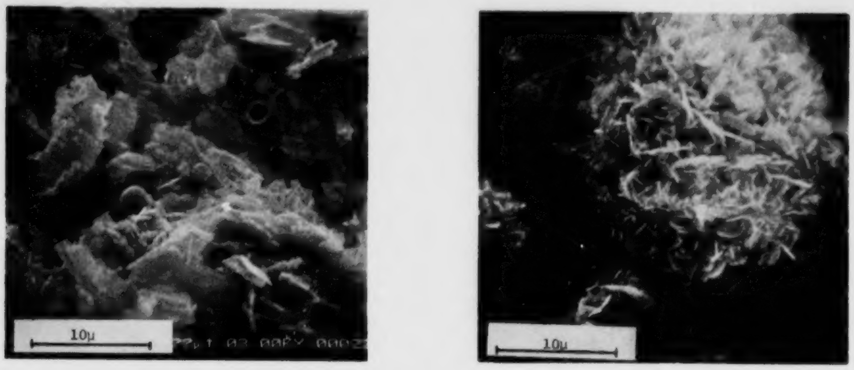
Phase III operation also demonstrated that addition of magnesium can assist in recovering from process upsets. After the scrubber had scaled on June 27 and 28, the magnesium concentration was increased, and subsaturated conditions were reestablished in the scrubber. A later scrubber inspection revealed that the deposited scale which was observed on June 28 had been dissolved completely. This implies that periodic addition of magnesium may be an alternative to system shut down for mechanical cleanup in certain instances where scale build-up is a problem.

4.2 Operating Problems

There were two operating difficulties of major significance encountered during Phase III. First, for about one week beginning July 12, operating personnel were unable to control the recirculating slurry solids concentration. Second, throughout the commercial lime operation, a continual liquid blowdown was required to maintain liquid levels in the system. The causes and implications of each process operating problem are described below.

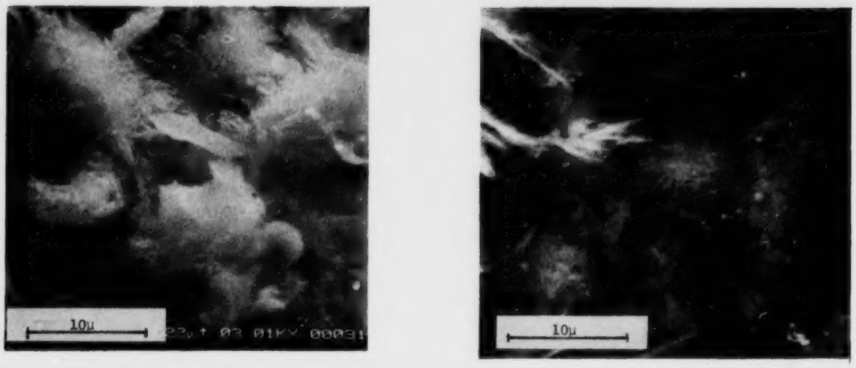
Solids Control. As mentioned in Section 3.0, the solids concentration in the recirculating slurry increased from about four percent to above 9 percent during the July 12 to July 19 time period. Basically, this problem was caused by a change in the settling characteristics of the solids in the clarifier. The clarifier overflow stream contained 4 to 5 percent solids during that week. This indicates that the solids settling rate in the clarifier had been reduced. Since the clarifier overflow stream is returned to the hold tank, this increased the solids concentration in the scrubbing loop.

The source of the solids settling problem was a change in the crystal characteristics. Figures 4-1 and 4-2 show electronmicrographs of selected solid samples taken during Phase III. The solids sampled on July 12 were composed of ill-defined needle-like structures as opposed to the large rosettes observed on July 5 and July 22 when solid-liquid separation was not a



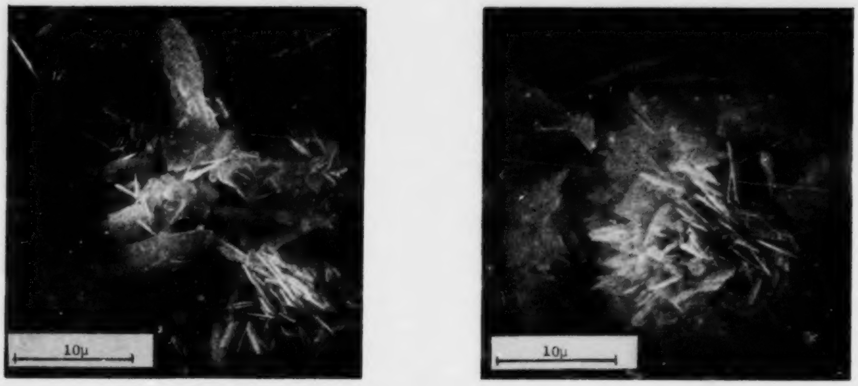
JUNE 28

JULY 5



JULY 12

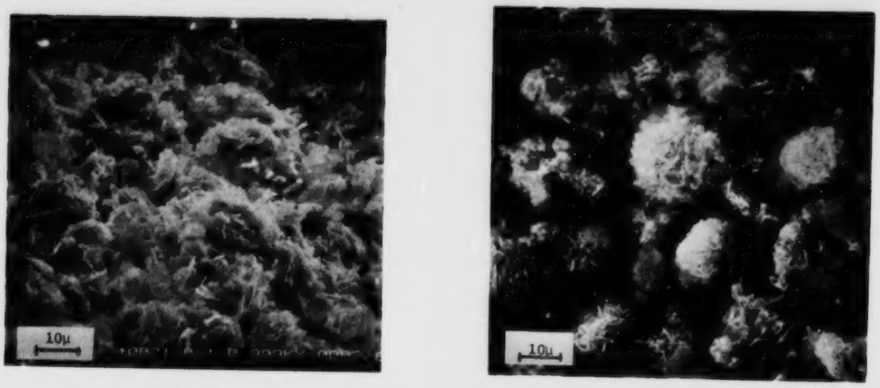
JULY 14



JULY 19

JULY 22

FIGURE 4-1 ELECTRON MICROGRAPHS OF SELECTED SOLIDS FROM PHASE III



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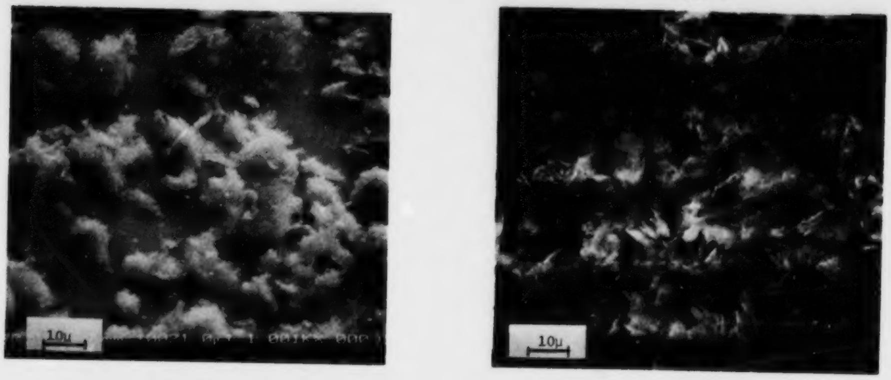
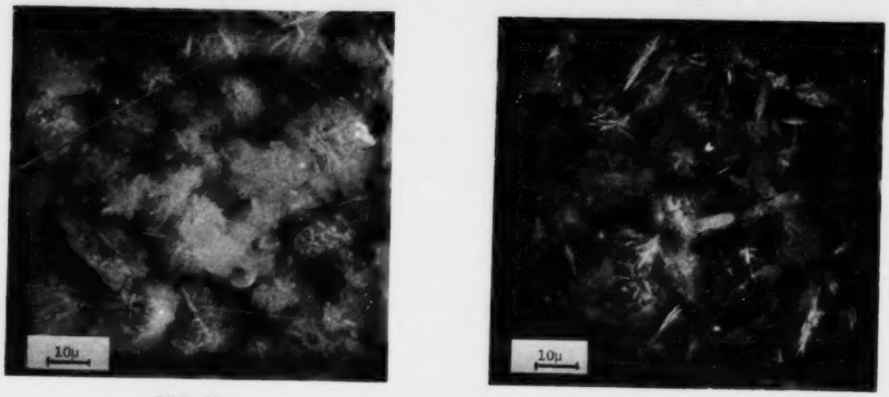
JULY 5



JULY 12

JULY 14



JULY 19

JULY 22

FIGURE 4-2 ELECTRON MICROGRAPHS FOR SELECTED SOLIDS FROM PHASE III

problem. On July 14, the size of the crystals had increased, but there still appeared to be some poorly defined, almost amorphous structures. This could possibly account for the poor solids settling characteristics.

The effect of crystal structure on solids settling rate is fairly obvious. The smaller solids with poorly defined crystalline structures (e.g., July 12 and July 14) would be expected to settle more slowly and to exhibit a lower settled bulk density than the larger spherical aggregates or rosettes such as those sampled on July 5. This can be seen from the settling curves presented in Figure 4-3. Each of these curves was generated for a 3 weight percent slurry of product solids.

The settling curves show definite differences in the settling rates of the solids during Phase III. By employing Figure 4-3, solids settling curves from the period of normal clarifier operation (July 1 and 6) can be compared to the settling curve obtained during the period of poor clarifier operation (July 14). A substantially lower initial settling rate and an increase in the volume of settled solids after 50 minutes is noted for the July 14 scrubber feed solid samples. The clarifier overflow solids from July 18 showed an even more retarded settling rate. This is probably due to both changes in the scrubber feed solids characteristics and classification of solid particles in the clarifier. The smaller particles would remain at the top of the clarifier and be returned to the scrubbing loop with the clarifier overflow. The clarifier overflow stream had become clear by July 21. The July 21 scrubber feed solids showed an increase in the density of the settled solids as compared to the July 14 solids. However, the settling rate and settled density were still less than those measured prior to the clarifier problem. By July 25, the scrubber feed solids settling curve was essentially the same as had been measured for the July 1 solids.

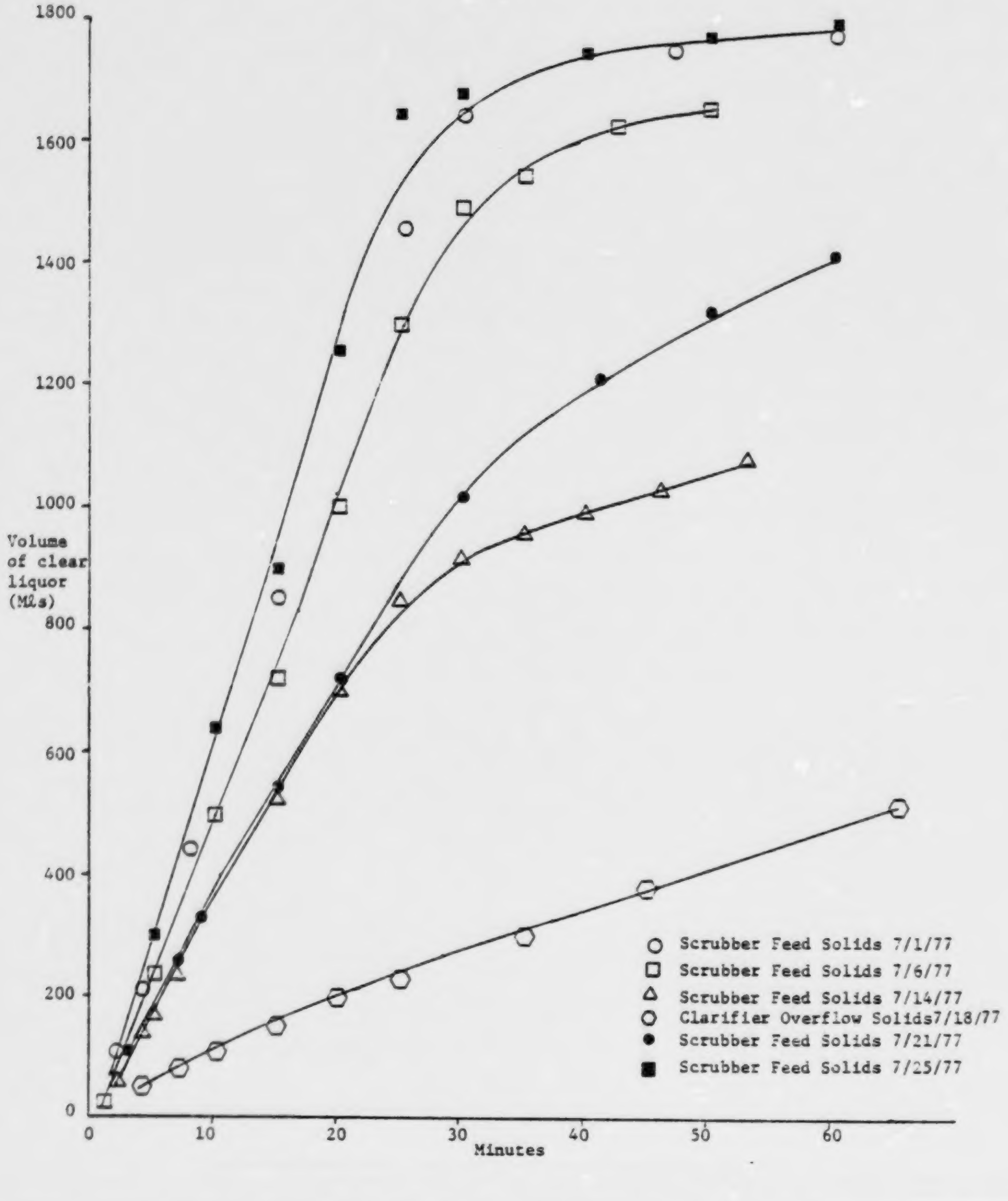


Figure 4-3. Settling curves for Phase III solids.

It is probable, that the magnesium concentration changes which occurred are at least partially responsible for the solid crystal structure changes seen in Figure 4-1 and 4-2. On July 12, the magnesium concentration in the scrubber feed liquor was measured at 184 mmoles per liter. This was the highest level recorded by Radian during the test program. Furthermore, data gathered by Combustion Engineering revealed that the magnesium concentration was in the 180-190 mmoles per liter range from July 9 through July 12.

This high magnesium concentration may have affected the calcium sulfite solids precipitation mechanism. Higher soluble sulfite concentrations would be associated with these higher magnesium concentrations. As a consequence, the calcium sulfite relative saturation near a dissolving lime particle would be higher. The increased relative saturation in turn, would promote additional nucleation which would result in smaller particles. From the micrographs in Figures 4-1 and 4-2, it appears that this occurred. Upon reduction of the magnesium concentration (to 120-130 mmole/liter by July 21 and 22), the size of the rosettes was increased.

In addition to the chemistry effects noted above, operating problems with the flocculant addition system may have been partially responsible for the poor clarifier operation. One problem with the system was the failure of a rupture disc in the flocculant feed line to the clarifier. This ruptured disc allowed water to mix with the flocculant in its storage tank. As a result, a smaller amount of flocculant, at a lower concentration, was fed to the mixing well of the clarifier. The lower concentration of floc in the clarifier may have reduced the clarifier efficiency, but it cannot explain the observed changes in crystal structure. Furthermore, correction of the floc addition system problems did not immediately reestablish clarifier efficiency.

A combination of process chemistry effects and flocculant addition system malfunctions probably led to the clarifier problems. It is significant to note here that no clarifying or solids control problems were recorded either with carbide or commercial lime with low magnesium concentrations.

Open Loop Operation. As was noted earlier, the system operated in an open loop throughout the commercial lime operating period (Phases II, III, IV, and V). The main reason for this, as explained in Appendix B, was the low lime solids concentration in the slurry received from AIRCO, LG&E's carbide and commercial lime supplier. Excess water in the lime additive slurry caused water balance problems. As a result, the clarifier overflow stream was periodically routed to the ash pond to control liquid levels. The average flow for this blowdown stream was about 75 liters per minute. The effect of this procedure was that the system operated in an open loop fashion. This blowdown, if mixed with the filter cake, would produce a 20-25 percent sludge. A 35-40 percent sludge was normally obtained from the vacuum filters and the blowdown was sent to the ash pond.

This problem has some important process chemistry implications. As was noted in Table 4-1, the amount of soluble sulfate leaving the system was roughly equivalent to the amount of solid sulfate leaving. Closing the loop in effect would increase all the soluble species concentrations as well as the fraction of sulfate in the solid phase. It is therefore possible that magnesium concentrations above 3000 ppm would be required to maintain system operability at Paddy's Run when operating in a closed loop mode with commercial lime. While the effect of a specific magnesium level on system operation would be expected to be dependent on a variety of system specific conditions, the same general trends demonstrated at Paddy's Run should apply to most other lime scrubbing systems.

APPENDIX D

PHASE IV
HOLD TANK MODIFICATIONS

1.0 SUMMARY

The objective of Phase IV testing was to determine the relative influence of the draft tube and the main reaction tank on scrubbing system operation. To accomplish this objective, two tests were conducted. First, the lime addition point was moved from the draft tube to a point opposite the draft tube in the main reaction tank. This change should have eliminated the draft tube effect. In the second test the lime additive point was moved back to the draft tube, and modifications were made to the system such that the main reaction tank was bypassed. This change reduced the total holding tank system volume from about 890,000 liters to about 130,000 liters.

Commercial lime was employed as the alkaline additive during these tests. Magnesium hydroxide was also added since earlier tests had shown that the Paddy's Run system could not be operated as designed with commercial lime as the only alkaline additive. Although magnesium addition did allow scale-free scrubber operation, different magnesium levels were required to maintain operable conditions during the two tests.

The same general trends relating magnesium concentration to system operation observed during Phase III were also seen during Phase IV. Basically, increases in magnesium concentration tended to decrease the fraction of sorbed SO_2 which was oxidized to sulfate, to decrease the soluble calcium concentration, and to decrease the gypsum relative saturation levels in all parts of the system. As long as the magnesium concentration was maintained sufficiently high, no calcium solids dissolved in the scrubber, and 99 percent removal of 2000 to 3000 ppm SO_2 from the flue gas was achieved. As the magnesium level dropped below that necessary to maintain sufficient liquid phase alkalinity, calcium solids began to dissolve in the scrubber, and the SO_2 removal efficiency decreased as a result. These trends were consistent with those observed in Phase III.

Although the trends remained the same, the actual magnesium concentrations required to maintain nonscaling conditions were different for the two different Phase IV test configurations. For instance, operation below 100 mmole/liter magnesium concentration appeared to be feasible in the "no draft tube" configuration. In fact, the system did not approach conditions which were saturated with respect to gypsum ($CaSO_4 \cdot 2H_2O$) until the magnesium concentration approached 70 mmole/liter. In the normal flow configuration employed during Phase III, saturated conditions were encountered as the magnesium concentration dropped into the 90-100 mmole/liter range.

Part of the difference in the required magnesium level may have been due to an unconfirmed increase in system blowdown during the latter stages of the draft tube elimination test. Unfortunately, the blowdown rate was not documented by system operators during this period. An increased liquid blowdown would increase the amount of sulfate exiting in the liquid phase thereby reducing the gypsum relative saturation in the scrubbing loop. When the magnesium was between 130 and 140 mmole/liter, the solid phase sulfate/total sulfur ratios (.045-.07) and gypsum relative saturations (less than 0.1 in the scrubber feed) were similar for operation both in the normal configuration and the no draft tube configuration. This result tends to support the possibility that increased blowdown assisted in maintaining operable scrubber conditions at the conclusion of the draft tube elimination test.

During the reduced hold tank residence time test, the oxidation fractions which were measured were higher than those noted in both Phase III and in the draft tube elimination test. For operation with magnesium levels in the 130-140 mmole/liter range the solid sulfate/total sulfur fraction was about 0.09.

At one point, operation at 120 mmole/liter magnesium showed apparent scaling conditions. The magnesium concentration was increased to about 140 mmole/liter to eliminate these conditions. To further document the scaling conditions at 120 mmole/liter magnesium concentration, the magnesium addition rate was lowered. Scaling conditions were not again encountered until less than 100 mmole/liter magnesium concentrations had been reached. This 100 mmole/liter magnesium concentration is similar to that level required to prevent scrubber scaling during Phase III. Although the oxidation fractions were higher in the reduced residence time test, the system was not operated for a sufficient period to determine the cause of the increase or the level of magnesium which would be required to maintain system reliability.

Increased agitation of the liquor in the draft tube may have been a source of the increased oxidation observed during the reduced residence time test. Because of fluctuations in draft tube liquid levels and a change in the flow pattern caused by sealing the bottom of the draft tube, aeration of the draft tube liquor was increased. This may have led to an increase in O_2 transfer in the draft tube and possibly higher oxidation.

A major concern during the hold tank modification test period was related to the waste solids characteristics. First, an alteration in crystal structure was anticipated. Second, possible changes in the amount of sulfate incorporated in the coprecipitated calcium sulfite-sulfate solids were of interest.

Differences in crystal structure were, in fact, seen during Phase IV. The elimination of the draft tube effect in combination with reduced magnesium concentrations produced calcium sulfite platelets similar to those produced in limestone systems. During the reduced residence time test with the lime entering the draft tube, the calcium sulfite crystals were in the form of rosettes which were typical of those produced during Phases I, II, and III. These observations are directionally consistent with the expected results.

Operation in the draft tube configuration with high magnesium concentrations at Paddy's Run was conducive to the formation of rosettes. Rosette formation is most likely in situations where supersaturations are high and nucleation with rapid precipitation on crystal nuclei surfaces is the predominant precipitation mechanism. Since lime dissolves much more quickly than limestone, high local supersaturations are characteristic of most lime systems, and rosettes are usually formed. In the draft tube, the scrubber effluent streams, whose soluble sulfite concentrations are high, are mixed with lime solids. As the lime dissolves, a rapid pH shift occurs in the region of the solid lime particles and high supersaturations result. Since magnesium sulfite is relatively more soluble than calcium sulfite, increases in magnesium concentration tend to increase soluble sulfite and decrease soluble calcium concentrations. The dissolution of lime in a liquor containing high concentrations of magnesium therefore can result in high localized calcium sulfite relative saturations. Since the lime was added into the draft tube during Phases I, II, III, and during the reduced residence time test in Phase IV, the formation of rosettes was not surprising.

In fact, the draft tube effect seemed to have more of an impact on the quality of the solids produced than did the reduced reaction volume. A slight increase in hold tank liquor calcium sulfite relative saturation was measured during the reduced volume test. However, with the lime added in the draft tube, little difference was noted between the crystal structure of solids formed in Phase III (large reaction volume) and the crystal structure of solids formed during the reduced residence time test in Phase IV.

Adding lime in the center of the main reaction tank eliminated the draft tube effect. Under these conditions the scrubber effluent streams are mixed with the bulk liquor in the hold tank prior to encountering the lime solids. In this mode the pH shifts were less severe and the sulfite supersaturation levels in the vicinity of individual lime particles should have been reduced. This is particularly true when lower magnesium concentrations were maintained. Thus, as a result of changing the lime additive point and reducing the magnesium concentration during Phase IV, crystal growth was the main precipitation mechanism and calcium sulfite platelets were formed.

The effects of these changes in crystal structure did have an impact on clarifier operation. Crystals which settle well and dewater easily are desirable. Laboratory experiments showed that the rosettes formed in Phase III, as well as in the reduced volume test, and the platelets formed during the draft tube elimination tests had similar bulk properties. The initial settling rate and settled density after one hour were slightly higher for the rosettes. However, during the transition from the rosettes to platelets, a period of poor solids settling was encountered. Clarifier efficiency was reduced, and the result was a loss of control of the slurry solids concentration. As larger platelets replaced the "transition" solids, solids control was reestablished. This emphasizes the need to understand the process chemistry related factors which control coprecipitate crystal formation.

Overall, the results from Phase IV indicate that both flow configurations can be employed successfully. As expected, some differences in solids crystal structure were noted. However, no evidence was found which indicated that the calcium sulfite precipitation rate affected the amount of sulfate incorporated into the calcium sulfite-sulfate coprecipitate. Comparison of results from the "no draft tube" test, where nucleation may have been reduced, with the Phase III ("draft tube") test, where nucleation predominated, does not show a dramatic difference in the calcium sulfite-sulfate coprecipitate formed. Although this does not prove conclusively that precipitation rate has no impact on the incorporation of sulfate into calcium sulfite/sulfate coprecipitate, it does tend to support the theory that formation of solid solution is an equilibrium phenomenon and not a kinetic one (1).

2.0 TEST APPROACH

The purpose of Phase IV testing was to observe the effect of two hold tank modifications on the LG&E scrubbing system. The first test involved elimination of the draft tube effect without altering the hold tank size. The second test reduced the hold tank residence time with the draft tube in place. This combination of tests was intended to determine whether the draft tube is a significant contributing factor to the successful performance of the LG&E scrubbing system.

2.1 Draft Tube Elimination

Elimination of the draft tube effect was achieved by relocating the lime additive's entry point. With the normal system configuration, the three scrubber effluent streams, the clarified liquor from the thickener-filter system, and the lime additive stream all enter the draft tube where they are well mixed before entering the main portion of the hold tank. For this test, the lime additive was added to the system at a point in the hold tank which was opposite the draft tube. Figure 2-1 indicates the flow scheme employed during the draft tube elimination test. The mixing of sulfur rich scrubber effluent streams with lime directly in the draft tube should tend to promote nucleation due to the relatively high local supersaturations which exist in the vicinity of dissolving lime particles. By adding the lime in the main hold tank, the lime would contact a liquor with a lower soluble sulfur concentration. This would tend to reduce the amount of nucleation occurring since the scrubber effluent liquor would first contact the hold tank liquor and be well mixed before encountering the lime slurry. Since calcium sulfite precipitation kinetics were thought to exert a possible influence over calcium sulfite-sulfate solid solution formation, this test was also designed with the intent of closely monitoring the solids characteristics.

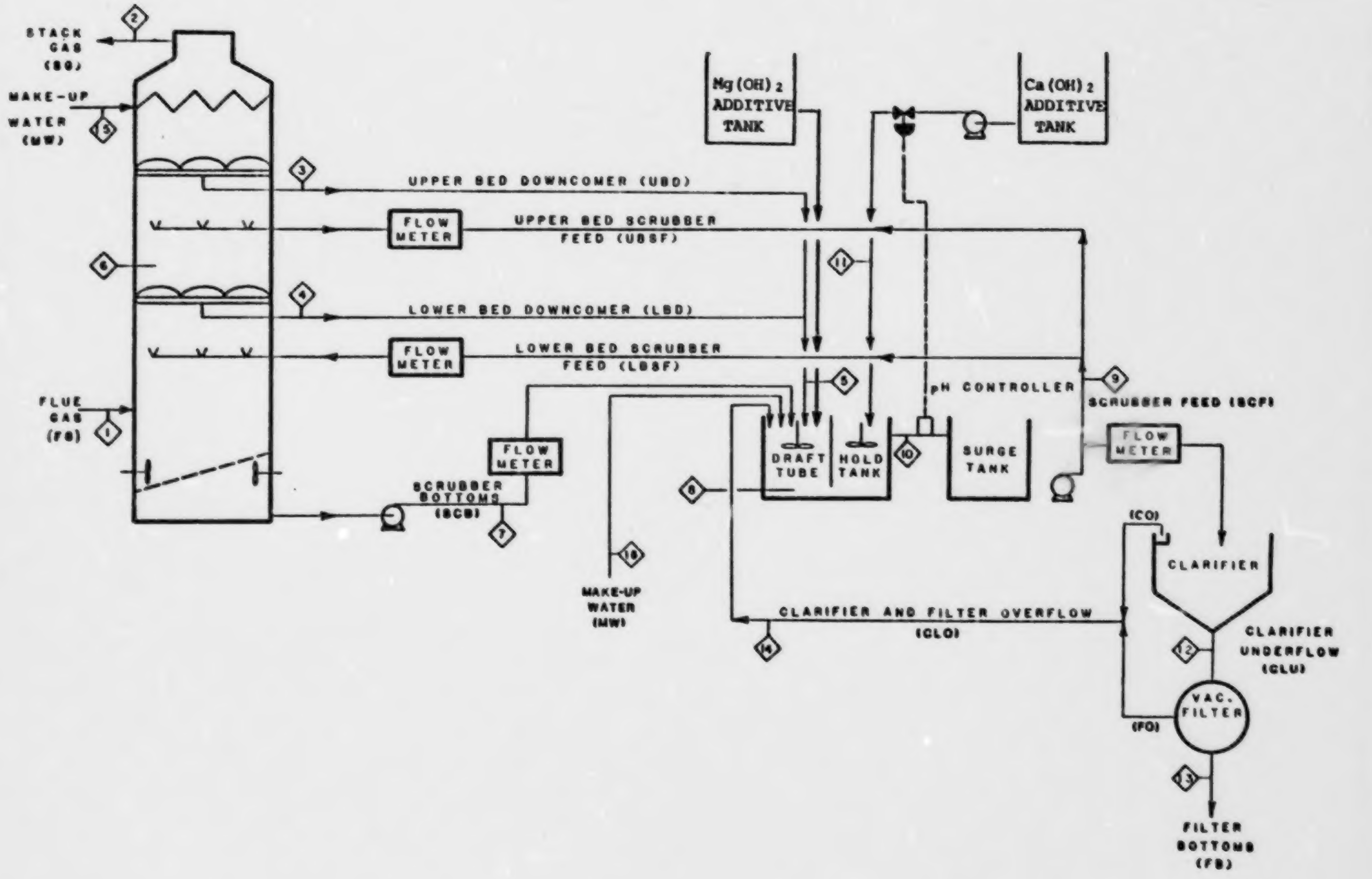

STACK GAS (SG)
2
MAKE-UP WATER (MW)
15
3
UPPER BED DOWNCOMER (UBD)
FLOW METER
UPPER BED SCRUBBER FEED (UBSF)
6
4
LOWER BED DOWNCOMER (LBD)
FLOW METER
LOWER BED SCRUBBER FEED (LBSF)
FLUE GAS (FG)
1
FLOW METER
SCRUBBER BOTTOMS (SCB)
7
MAKE-UP WATER (MW)
16
Mg(OH)2 ADDITIVE TANK
Ca(OH)2 ADDITIVE TANK
11
5
8
DRAFT TUBE
HOLD TANK
10
pH CONTROLLER
SURGE TANK
9
SCRUBBER FEED (SCF)
FLOW METER
(CO)
CLARIFIER
CLARIFIER AND FILTER OVERFLOW (CLO)
14
CLARIFIER UNDERFLOW (CLU)
12
VAC. FILTER
(FO)
13
FILTER BOTTOMS (FB)

Figure 2-1. Hold tank modifications - draft tube elimination.

2.2 Reduced Hold Tank Residence Time

In the second hold tank modification test, the hold tank residence time was reduced from about 35 minutes (890,000 liters capacity) to approximately 5 minutes (130,000 liters capacity). This was accomplished by sealing the bottom of the draft tube and routing the draft tube effluent directly to the surge tank. In this manner, the main hold tank was effectively eliminated from the scrubbing loop, and the solid phase residence time in the scrubbing loop was reduced from about 1360 minutes to 350 minutes. Figure 2-2 shows the process configuration used during this test.

The purpose of running this test was to document the effect of the large hold tank on system performance. In addition to determining the feasibility of operating with a relatively small reaction tank, this test was designed to assist in determining the predominant precipitation mechanism in the LG&E system. If a large amount of precipitation occurred through nucleation in the draft tube, then reducing the total hold tank volume should not have a major impact on system operation. On the other hand, if a significant amount of the precipitation was normally accomplished by crystal growth, then elimination of the hold tank should have led to noticeable changes in process variables such as the liquid phase calcium sulfite relative saturation. A comparison of these levels for Phases III and IV was expected, at least qualitatively, to identify the important precipitation mechanisms and the relative importance of the draft tube versus the main reaction tank.

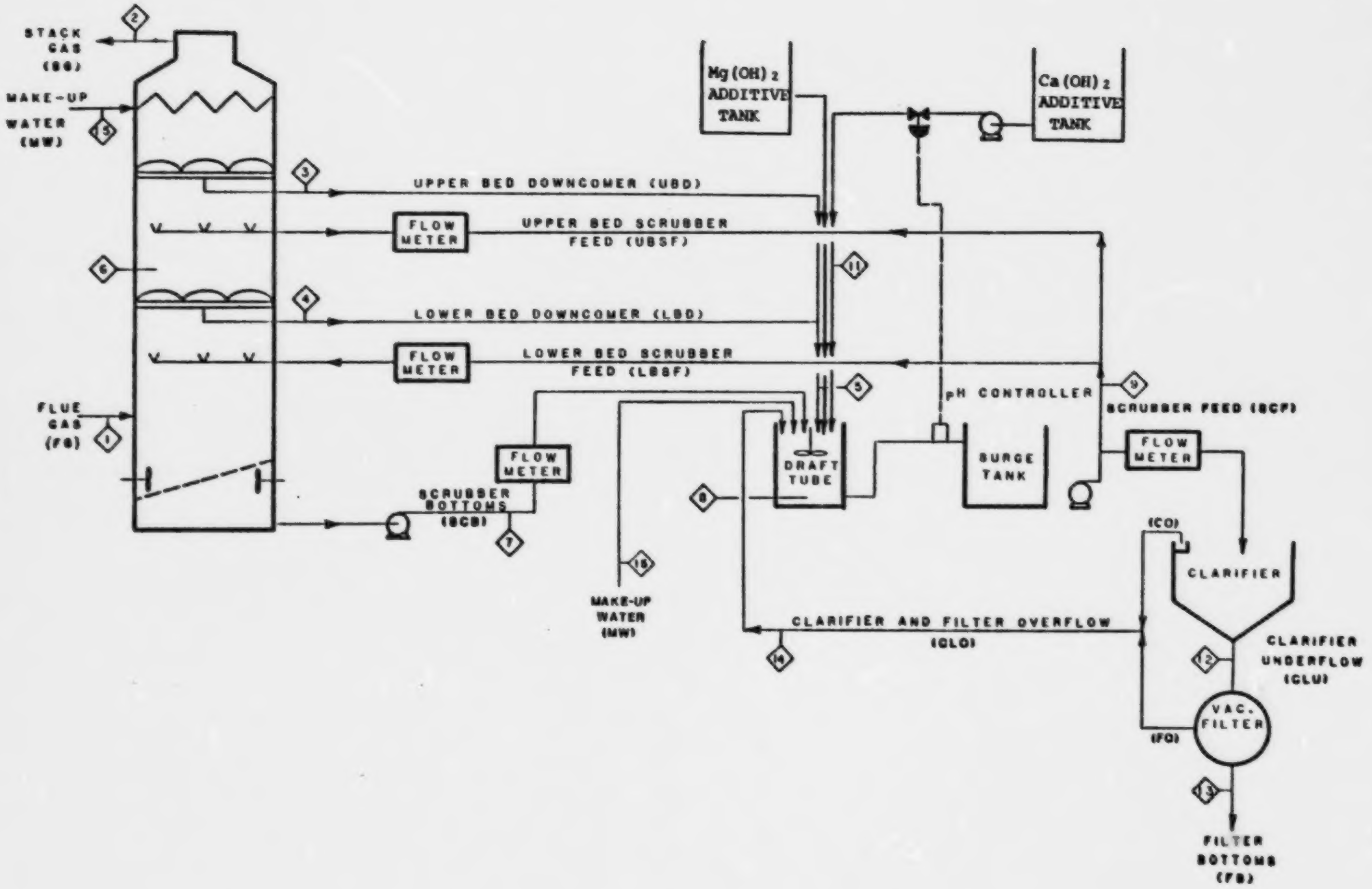

STACK GAS (SG)
2
MAKE-UP WATER (MW)
15
6
FLUE GAS (FG)
1
3
UPPER BED DOWNCOMER (UBD)
FLOW METER
UPPER BED SCRUBBER FEED (UBSF)
4
LOWER BED DOWNCOMER (LBD)
FLOW METER
LOWER BED SCRUBBER FEED (LBSF)
FLOW METER
SCRUBBER BOTTOMS (SCB)
7
Mg(OH)2 ADDITIVE TANK
Ca(OH)2 ADDITIVE TANK
11
5
pH CONTROLLER
9
SCRUBBER FEED (SCF)
DRAFT TUBE
SURGE TANK
8
FLOW METER
16
MAKE-UP WATER (MW)
(CO)
CLARIFIER
CLARIFIER AND FILTER OVERFLOW (CLO)
14
12
CLARIFIER UNDERFLOW (CLU)
VAC. FILTER
(FO)
13
FILTER BOTTOMS (FB)

Figure 2-2. Hold tank modifications - five minute residence time.

2.3 Magnesium Addition

The two hold tank modification tests were originally intended to be conducted at low soluble magnesium concentrations. However, as is discussed in Appendix C, magnesium addition was needed to maintain system operability. Therefore, the hold tank modifications were conducted with magnesium addition.

3.0 RESULTS

This section discusses the process and analytical results obtained during Phase IV operation. Figure 3-1 summarizes the important process and analytical data collected during Phase IV. General summaries of the significant results of the Phase IV tests are furnished in the following two subsections. Problems and data inconsistencies are noted.

3.1 Process Data

Phase IV testing was conducted from July 25 to August 24. The draft tube elimination test lasted from July 25 to August 8, and the reduced hold tank volume test ran from August 16 to August 24. Table 3-1 summarizes the process measurements made during both tests.

During Phase IV, only two scrubber system outages were noted. Figure 3-1 shows that the first one was on August 2, and the second occurred between August 8 and August 16. The August 2 down time was required to repair nozzles on the lower scrubber feed header. Table 3-1 indicates that the scrubber bottoms flow rate increased from 4770 liters/minute at the beginning of the run to 5900 liters/minute on August 1. Scrubber inspection revealed that several nozzles were either damaged or had become detached from the spray header. After repairs were made, the scrubber bottoms rate was reduced, but it did not return to the rate measured in previous test phases. During the second outage between August 8 and 16, hold tank modifications were made which reduced the total reaction volume from 890,000 liters to 130,000 liters. Other than these two outages the scrubbing system operated continuously during Phase IV.

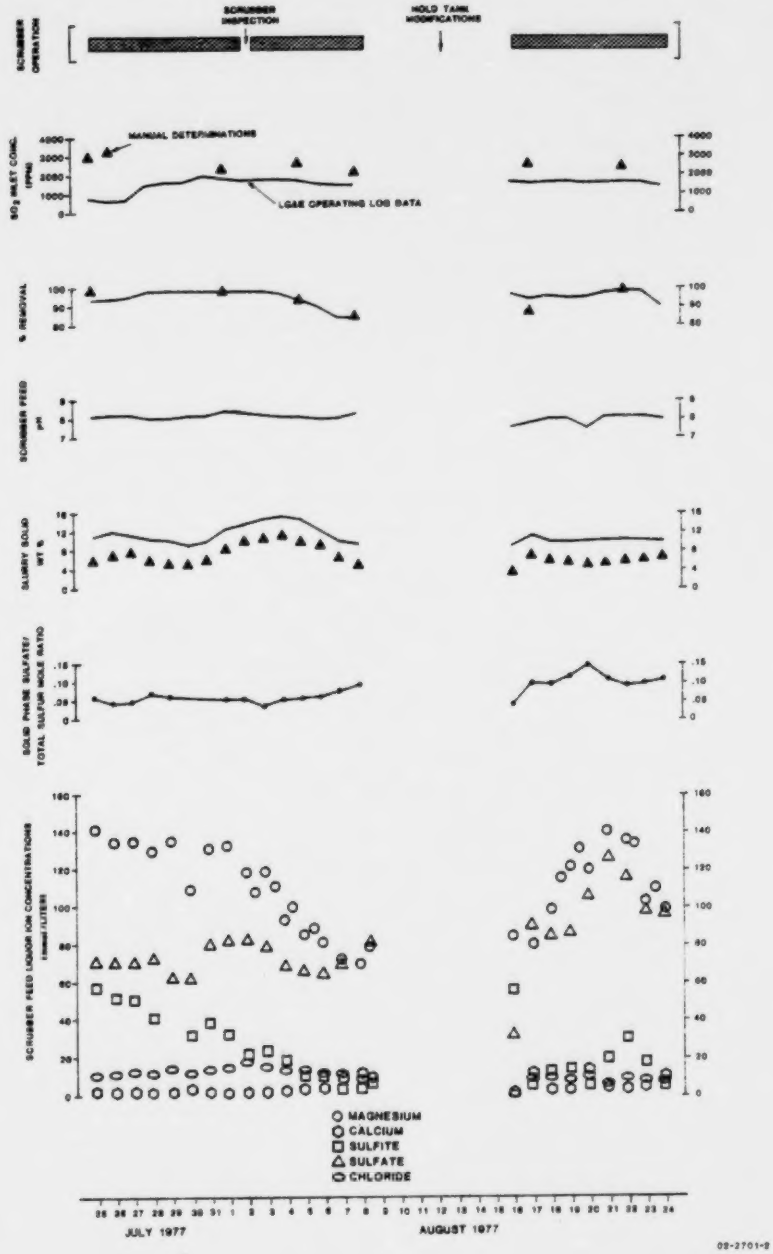


Figure 3-1. Phase IV operating summary.

TABLE 3-1. PHASE IV - PROCESS MEASUREMENTS

	Measure effect of draft tube elimination - Test #15										Measure effect of reduced hold tank volume - Test #16						
	July 25	July 26	July 27	July 28	July 29	Aug. 1	Aug. 3	Aug. 4	Aug. 5	Aug. 8	Aug. 16	Aug. 17	Aug. 18	Aug. 19	Aug. 22	Aug. 23	Aug. 24
Flue Gas (Nm^3/hr) (dry)	169,000	158,000	-	-	-	190,000	-	-	185,000	183,000	-	158,000	156,000	156,000	170,300	-	-
SO$_2$ inlet (ppm)	3,040	3,430	-	-	2,930[1]	2,350	2,300[1]	2,810[1]	2,660	2,090	2,440[1]	2,690	2,370[1]	2,670[1]	2,400	2,320[1]	2,200[1]
SO$_2$ outlet (ppm)	13	-	-	-	20[1]	15	20[1]	90[1]	198	312	50[1]	282	105[1]	190[1]	13	70[1]	180[1]
SO$_2$ removal efficiency (%)	99				99	99	99	97	93	85	98	89	96	93	99	97	92
Scrubber feed (ℓpm)	26,500 →	→	→	→	→	→	→	→	26,100	26,300	25,700 →	→	→	→	→	→	→
Upper bed	13,200 →	→	→	→	→	→	→	→	→	→	12,900 →	→	→	→	→	→	→
Lower bed	13,200 →	→	→	→	→	→	→	→	12,800	13,000	12,800 →	→	→	→	→	→	→
L/G (liters/Nm^3)	9.4	10.1	-	-	-	8.4	-	-	8.5	8.6	-	9.8	9.9	9.9	9.1	-	-
Scrubber feed pH	8.0	8.1	8.3	8.3	7.4	8.1	8.0	8.0	8.0	8.5	7.7	7.0	7.2	7.9	7.9	7.8	7.2
Slurry solids content (% wt)	6.2	7.2	7.8	6.0	5.8	8.2	10.2	11.4	10.3	5.6	3.4	6.5	5.9	5.5	5.8	6.2	6.5
Scrubber bottoms (ℓpm)	4,770 →	→	→	→	→	5,900	4,770 →	→	5,900 →	→	5,110 →	→	→	→	5,000 →	→	→
Clarifier feed (ℓpm)	719	757	644	757	757	719	757	-	360	750	757 →	→	→	→	→	→	→
Clarifier overflow (ℓpm)	-	-	-	-	-	530	-	-	-	-	-	-	-	582	-	-	-
Filter Bottoms (kg/min)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Lime additive (ℓpm)	291	-	269	252	244	244	260	277	277	171	334	269	227	244	337	272	217
Makeup water (ℓpm)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

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[1] Estimated from DuPont data

Since mechanical modifications were being tested in Phase IV, process variable levels similar to those established in Phases II and III were sought. The same set points for boiler load (35 MW), scrubber feed rate, (26,500 liters/minute) recirculating solids content (∿6 percent), and pH (8.0), for example, were desired. However, some deviation from these set points occurred.

One variable which fluctuated substantially during the testing period was the flue gas rate. Although the boiler rate was never intentionally altered, the excess air rate or possibly air leakage caused flue gas rates to vary between 156,000 Nm^3/hr and 190,000 Nm^3/hr. Since the liquid rate was relatively constant, the L/G changed from 10.1 to 8.4 liters/Nm^3.

Basically, the changes in L/G mentioned above did not seem to impact system operation as much as the magnesium concentration. The magnesium content of the scrubbing liquor seems to be the variable with the most influence on SO_2 removal efficiency. This effect is shown in Figure 301. Inlet gas SO_2 loadings between 2000 and 3500 were measured while the SO_2 removal efficiency ranged from 85 to 99 percent. Generally, lower magnesium loadings resulted in lower removal efficiencies.

A major discrepancy between the inlet gas SO_2 concentrations determined by the DuPont and manual analysis for July 25 and 26 should be noted here. A leak in the DuPont inlet sample line was found on July 28. After the problem was corrected, manual and DuPont measurements were more consistent. However, a consistent variance between the two types of measurements is evident. This is due probably to an error in the DuPont calibration. Since the difference is fairly constant, the DuPont results after July 28 do seem to reflect system operating trends.

The reduction in magnesium concentration which began on August 1 had originally been planned to compare the effect of magnesium on system operation with no draft tube. However, the timing of the magnesium concentration reduction was affected by a solids control problem which also began on August 1. A similar solids control problem had been experienced in Phase III, and resolution of the problem had been accompanied by a reduction in soluble magnesium concentration. Therefore, the magnesium addition rate was reduced beginning on August 1.

The solids control problem here, as in Phase III, was caused by poor solid-liquid separation in the clarifier. On August 1, the clarifier overflow stream registered 6.3 percent solids while the clarifier underflow measured only 8.8 percent solids. As a result, the solids in the scrubbing loop increased from about 6 to 10-11 percent between August 3 and 6. This trend is shown in Table 3-1 and in Figure 3-1. Clarifier efficiency and solids control were restored on August 7 while draft tube elimination testing was in progress.

During the early stages of the reduced hold tank volume test, some pH control problems were encountered. The pH control sensor was moved from the overflow line between the draft tube and surge tank into the surge tank. This stabilized the control somewhat, but the pH was more sensitive to system operating changes throughout the reduced volume testing.

As was the case in all commercial lime testing, blowdown of clarifier overflow was necessary to maintain system liquor levels. Roughly 80 liters/minute of the overflow stream was routed to the ash pond during Phase IV.

3.2 Analytical Data

The analytical data gathered during Phase IV is presented in Tables 3-2 and 3-3. Table 3-2 furnishes a chemical data summary for the draft tube elimination test. Table 3-3 presents the same type of data for the reduced hold tank residence time test.

During the draft tube elimination test, some of the same general relationships which had been observed in Phase III were noted. The magnesium concentration ranged from 142 mmole/liter down to 70 mmole/liter. The solid sulfate/sulfite mole fraction was generally lower at higher magnesium concentrations, ranging from 0.049 to 0.096. The amount of calcium dissolution remained small when the magnesium content was above 100 mmole/liter. The gypsum relative saturation remained below 1.0 except on August 8 when all scrubber effluent streams were supersaturated. This occurred at a magnesium concentration of 70 mmole/liter. Although the system appeared to remain operable at liquid phase magnesium loadings of 70-80 mmoles per liter, the significance of this result relative to what was observed in Phase III may be clouded by the existence of clarifier overflow blowdown rates which were possibly higher than normal. Unfortunately, these higher than average blowdown rates were not quantitatively verified during Phase IV.

Overall, the results from the reduced hold tank volume test were very interesting. Relative to base case conditions (large hold tank), the calcium sulfite relative saturation in the scrubber feed liquor was slightly higher during the low residence time test. This is consistent with what would be expected.

TABLE 3-2. CHEMICAL DATA SUMMARY FOR DRAFT TUBE ELIMINATION TESTING

Sample identification			Slurry Properties			Liquid analyses (mmol/liter)							Solid analyses (mmol/g)						Computer results		
Date	Stream[1]	Time	pH	Temp (°C)	% Solids	Ca^{++}	Mg^{++}	Na^{+}	Cl^{-}	$CO_3^{=}$	$SO_3^{=}$	$SO_4^{=}$	Ca^{++}	Mg^{++}	$CO_3^{=}$	$S.SO_4^{=}$	T.S.	Ox Frac	$CaSO_3RS$	$CaSO_4RS$	P^*SO_2(PPM)
7-25	SCF	8:55	8.0	50	6.2	.93	142.	2.1	10.5	7.67	56.7	69.9	7.70	.0	.532	.33	6.67	.049	2.27	.03	
	LBD	9:30	6.6	53	-	.86	151.	-	22.0	-	69.0	77.5							1.73	.03	
	UBD	9:20	7.2	52	-	.83	141.	-	12.2	-	55.9	71.9							1.85	.03	
	SCB	9:05	6.0	51	-	1.50	145.	-	31.5	-	86.9	84.6							2.15	.05	
	DTE	9:40	8.1	47	-	1.56	131.	-	20.6	-	46.8	72.4							3.64	.05	
	CLO	9:30	7.7	30	-	1.03	132.	-	17.5	-	41.5	81.4							2.45	.04	
	CLU	9:30	8.7	30	26.3	1.02	131.	2.03	18.6	4.30	39.2	81.0	7.76	.0	.518	.37	6.52	.057	2.40	.04	
	LA	9:40	12.1	25	12.0	14.8	-	-	1.43	-	1.07	.11	12.9	.0					-	-	-
	MgA	9:30	10.5	20	53.3	-	26.3	-	71.5	-	.19	.95		15.93					-	-	-
	MW	9:30	8.3	25	-	1.34	.50	-	1.03	-	.24	.99							-	-	-
7-26	SCF	8:20	8.1	49	7.2	.97	136.	-	11.4	-	51.9	71.1	7.74	.0	.57	.30	6.69	.045	2.31	.03	.0007
	LBD	8:40	6.6	53	-	1.41	129.	-	12.0	-	67.4	65.7							2.28	.04	.75
	UBD	8:40	7.3	52	-	1.05	140.	-	21.3	-	53.2	79.8							-	-	.028
	SCB	8:30	6.5	50	-	1.22	134.	-	12.6	-	80.8	65.9							2.78	.03	1.2
7-27	SCF	9:10	8.3	49	7.8	.85	136.	-	12.7	-	51.0	69.2	7.65	.01	-	.32	6.57	.049	2.03	.03	.0003
	LBD	8:50	6.8	51	-	1.3	137.	-	14.0	-	65.3	72.2							2.29	.03	.29
	UBD	8:55	7.3	50	-	1.0	135.	-	12.0	-	53.7	70.1							2.94	.04	.026
	SCB	9:15	6.3	50	-	1.2	144.	-	13.7	-	81.7	72.6							3.04	.04	2.3
	DTE	9:20	7.0	47	-	1.3	133.	-	13.3	-	58.3	67.3							2.32	.04	.091
7-28	SCF	8:45	8.3	48	6.0	1.13	130.	-	11.7	-	41.0	72.6	7.33	.23	-	.46	6.20	.074	2.37	.04	.0002
	LBD	8:35	6.9	52	-	1.22	133.	-	12.5	-	53.9	73.6							2.59	.05	.16
	UBD	8:25	7.3	51	-	1.34	132.	-	14.2	-	42.0	74.9							2.53	.04	.020
	SCB	8:50	6.1	52	-	1.17	141.	-	14.9	-	72.5	68.7							1.73	.04	4.1
7-29	SCF	8:40	7.4	52	5.8	1.0	135.	-	14.4	-	58.1	63.3	7.79	-	.77	.42	6.58	.064	2.40	.03	.025
	LBD	8:55	6.4	55	-	.96	138.	-	14.4	-	76.1	70.7							1.86	.03	1.9
	UBD	9:00	6.9	53	-	.99	138.	-	14.6	-	59.8	69.8							2.15	.03	.19
	SCB	8:45	6.1	53	-	.74	150.	-	14.2	-	85.7	75.1							1.16	.02	5.2
7-30	SCF	10:00	7.7	50	5.5	1.91	109.	-	12.2	-	32.9	61.1							3.67	.07	.003
	SCB	10:05	6.3	50	-	2.08	131.	-	13.5	-	54.3	83.4							3.14	.08	1.5
7-31	SCF	10:00	7.9	51	6.1	1.52	132.	-	14.3	-	38.0	79.4							2.86	.06	.001
	SCB	10:05	6.1	51	-	1.85	134.	-	14.2	-	64.3	86.5							2.51	.07	3.6
8-1	SCF	9:30	8.1	50	8.2	.96	133.	2.58	14.8	6.24	33.5	82.5	7.61	.09	.52	.37	6.73	.055	1.67	.04	.0004
	LBD	9:10	6.4	52	-	1.43	134.	-	15.0	-	52.1	83.6							2.21	.06	1.1
	UBD	9:10	7.0	52	-	1.23	133.	-	14.3	-	40.3	78.6							2.14	.05	.074
	SCB	9:40	6.1	49	-	2.01	133.	-	14.2	-	63.5	82.0							2.81	.08	3.3
	DTE	9:45	6.6	47	-	1.51	129.	-	13.8	-	46.1	78.1							2.64	.06	.36
	CLO	9:30	6.8	30	6.3	1.38	134.	-	14.0	-	41.4	88.5							2.81	.06	.058
	CLU	9:30	7.7	30	8.8	1.65	130.	2.56	13.7	7.61	24.6	92.3							2.69	.08	.0006
	LA	9:30	12.4	25	11.0	-	-	-	-	-	-	-							-	-	-
	MgA	9:30	10.5	25	54.2	-	-	-	-	-	-	-							-	-	-
	MW	9:30	7.7	25	-	1.52	.61	-	1.30	-	.05	1.44							-	-	-
8-2	SCF	8:25	8.1	49	9.8	2.05	117.	-	17.2	-	22.1	83.3	7.38	.04	-	.36	6.62	.055	2.79	.10	.0003
	SCB	8:30	5.6	48	-	3.07	120.	-	15.8	-	40.1	88.4							1.56	.16	8.7
8-2	SCF	15:15	8.2	47	-	2.21	109.	-	13.1	-	-	-							-	-	-
	SCB	15:20	6.0	47	-	3.18	113.	-	-	-	-	-							-	-	-

(Continued)

TABLE 3-2. CHEMICAL DATA SUMMARY FOR DRAFT TUBE ELIMINATION TESTING (Continued)

Sample identification			Slurry properties			Liquid analyses (mmol/liter)							Solid analyses (mmol/g)						Computer results		
Date	Stream[1]	Time	pH	Temp (°C)	% Solids	Ca^{++}	Mg^{++}	Na^{+}	Cl^{-}	$CO_3^{=}$	$SO_3^{=}$	$SO_4^{=}$	Ca^{++}	Mg^{++}	$CO_3^{=}$	S.$SO_4^{=}$	T.S.	Ox Frac	$CaSO_3$RS	$CaSO_4$RS	$P^{*}SO_2$(PPM)
8-3	SCF	8:35	8.0	47	10.2	1.54	117.	-	14.9	-	25.3	77.9	7.64	.05	-	.27	6.72	.04	2.39	.07	.0004
	LBD	8:25	6.4	51	-	1.97	120.	-	14.2	-	37.1	80.7							2.53	.09	.75
	UBD	8:25	7.0	50	-	1.94	118.	-	13.5	-	31.1	76.3							3.02	.08	.055
	SCB	8:40	6.1	50	-	2.01	120.	-	13.9	-	44.7	82.2							2.25	.09	2.5
	SCF	14:10	8.0	47	-	1.74	111.	-	12.9	-	20.7	79.5							2.37	.08	.0004
8-4	SCF	8:40	8.0	48	11.4	2.13	93.8	-	13.2	-	18.0	67.6	7.64	-	-	.37	6.94	.053	2.89	.10	.0004
	LBD	8:20	5.5	51	-	4.22	99.8	-	13.1	-	36.2	71.3							1.73	.21	12.
	UBD	8:25	5.9	51	-	2.86	101.	-	13.5	-	26.8	72.8							1.73	.14	3.0
	SCB	8:45	5.6	51	-	4.14	92.9	-	12.1	-	36.9	65.8							2.14	.20	9.9
	SCF	15:20	8.0	50	-	1.90	100.	-	13.0	-	22.1	66.8							2.87	.08	.0005
8-5	SCF	9:05	8.0	50	10.3	2.35	85.9	-	12.9	-	11.3	66.4	7.62	-	-	.393	6.86	.057	2.23	.12	.0003
	LBD	8:50	5.4	51	-	7.55	89.7	-	13.5	-	30.3	71.0							2.94	.40	15.
	UBD	9:00	5.9	51	-	4.10	78.1	-	11.9	-	22.5	59.7							2.30	.21	3.1
	SCB	9:10	5.5	49	-	6.32	90.7	-	14.1	-	28.9	70.9							2.26	.33	9.1
	SCF	15:05	8.0	49	-	2.39	88.0	-	12.8	-	10.2	68.1							2.00	.13	.0002
	SCB	15:10	5.5	48	-	6.88	89.7	-	14.3	-	36.3	63.9							3.09	.33	12.
8-6	SCF	7:50	7.7	50	8.8	3.09	81.5	-	12.4	-	9.29	65.1	7.48	-	-	.45	6.82	.066	2.49	.17	.0009
	SCB	7:55	5.5	50	-	7.97	83.8	-		-	26.9	71.2							2.67	.44	9.5
8-7	SCF	9:50	7.7	50	6.7	9.15	72.4	-	11.5	-	4.48	69.6	7.62	.04	-	.54	6.95	.078	3.61	.58	.0004
	SCB	9:55	5.3	50		14.9	73.6	-	8.7	-	19.2	72.7							2.49	.90	11.
8-8	SCF	9:30	8.5	51	5.6	11.5	70.1	2.75	7.88	-	3.58	69.8	7.71	.10	-	.63	6.93	.091	3.67	.74	.000008
	LBD	9:00	5.1	51	-	19.2	77.2	-	6.79	-	17.9	78.8							1.86	1.19	17.
	UBD	9:00	5.1	51	-	16.8	75.4	-	6.44	-	14.0	76.5							1.33	1.07	13.
	SCB	9:35	5.2	50	-	19.5	77.1	-	5.82	-	17.6	79.5							2.32	1.22	13.
	SCF	12:30	7.8	49	5.4	8.77	78.2	-	9.34	-	4.97	76.1	7.64	.0	-	.66	6.88	.096	3.70	.56	.0003
	LBD	12:25	5.2	50	-	15.6	81.8	-	9.43	-	20.1	80.3							2.10	.96	15.
	UBD	12:25	5.4	50	-	13.3	80.1	-	9.28	-	16.0	77.8							2.23	.83	7.1
	SCB	12:35	5.6	53	-	12.7	75.9	-	11.5	-	18.8	70.7							3.56	.74	5.0
	CLO	12:20	8.3	30	-	8.3	77.2	-	9.78	-	3.96	72.7							3.59	.57	.00002
	CLU	12:20	8.6	30	9.7	8.1	74.6	-	9.61	-	2.87	77.3	7.66	.10	-	.64	6.89	.093	2.64	.60	.000005
	LA	12:30			12.4								13.2								
	MgA	12:30			54.9																
	FB	12:30			31.9																

[1] Stream Identification
SCF - Scrubber Feed
LBD - Lower Bed Downcomer
UBD - Upper Bed Downcomer
SCB - Scrubber Bottoms
DTE - Draft Tube Effluent
CLO - Clarifier Overflow
CLU - Clarifier Underflow
LA - Lime Additive
MgA - Magnesium Additive
MW - Makeup Water

TABLE 3-3. CHEMICAL DATA SUMMARY FOR REDUCED HOLD TANK VOLUME TESTING

Sample identification			Slurry properties			Liquid analyses (mmol/liter)							Solid analyses (mmol/g)						Computer results		
Date	Stream[1]	Time	pH	Temp (°C)	% Solids	Ca^{++}	Mg^{++}	Na^{+}	Cl^{-}	CO$_3^{=}$	SO$_3^{=}$	SO$_4^{=}$	Ca^{++}	Mg^{++}	CO$_3^{=}$	S.SO$_4^{=}$	T.S.	Ox Frac	CaSO$_3$RS	CaSO$_4$RS	P*SO$_2$(PPM)
8-16	SCF	14:20	7.7	50	3.4	.95	95.0	-	.85	-	56.5	33.0	7.65	-	-	.26	6.43	.04	2.87	.02	.006
	LBD	14:15	6.6	53	-	.76	97.7	-	-	-	71.4	39.4							1.93	.02	.87
	UBD	14:15	7.0	53	-	.72	96.6	-	-	-	57.1	32.3							1.94	.01	.13
	SCB	14:30	6.2	50	-	.80	100.	-	-	-	77.5	44.7							1.62	.02	3.7
8-17	SCF	8:30	7.0	49	6.5	12.3	90.0	-	9.04	-	4.32	90.7	7.50	-	-	.66	6.68	.10	3.41	.84	.007
	LBD	9:00	4.8	53	-	22.8	87.2	-	8.08	-	22.0	93.4							1.23	1.46	41.
	UBD	8:50	5.3	53	-	16.4	72.7	-	7.37	-	13.9	73.0							1.93	1.02	8.0
	SCB	8:35	5.0	50	-	19.1	88.9	-	8.73	-	20.0	95.3							1.54	1.26	23.
	LA	10:20	-	-	10.6	-	-	-	-	-	-	-									
8-18	SCF	8:25	7.2	49	5.9	4.22	98.3	-	8.98	2.64	11.3	83.6	7.79	-	-	.63	6.74	.09	3.24	.25	.009
	LBD	8:15	5.4	53	-	9.75	99.7	-	6.55	2.08	26.1	86.5							2.26	.57	15.
	UBD	8:45	5.9	52	-	5.85	97.4	-	8.50	4.25	18.9	86.2							2.53	.35	3.4
	SCB	8:35	5.1	50	-	7.49	99.7	-	6.93	3.12	24.2	88.6							.94	.46	31.
	SCF	13:30	7.6	49	-	2.58	113.	-	6.15	-	20.5	87.7							3.24	.13	.01
	LBD	13:35	5.8	49	-	5.16	115.	-	5.18	-	35.8	92.6							3.23	.28	8.4
8-19	SCF	8:30	7.9	49	5.5	4.55	122.	-	8.38	-	12.8	107.	7.67	-	-	.82	6.84	.12	3.53	.28	.0004
	LBD	8:25	5.3	52	-	9.68	124.	-	8.01	-	29.6	110.							1.86	.60	16.
	UBD	8:30	5.9	52	-	6.24	126.	-	8.24	-	20.0	110.							2.45	.39	2.0
	SCB	8:25	5.5	48	-	8.84	134.	-	9.08	-	29.7	123.							2.54	.57	9.4
	SCF	13:10	7.5	47	-	5.37	133.	-	6.96	-	13.2	118.							3.95	.34	.002
	LBD	13.15	5.8	49	-	9.87	134.	-	6.71	-	27.6	123.							4.33	.62	3.7
8-20	SCF	8:45	7.6	50	5.0	14.0	121.	-	10.4	-	5.63	126.	7.72	-	-	1.00	6.75	.15	4.33	1.00	.0006
	LBD	9:00	5.4	50	-	22.8	123.	-	6.74	-	20.3	132.							3.53	1.59	7.9
8-21	SCF	10:15	7.7	51	5.4	3.56	141.	-	6.81	-	18.9	116.	8.05	-	-	.74	6.65	.11	3.43	.21	.001
	SCB	10:25	5.9	50	-	6.25	141.	-	9.49	-	32.9	124.							3.62	.38	3.3
8-22	SCF	8:45	7.9	51	5.8	1.61	136.	4.60	10.1	6.16	30.9	95.8	7.68	-	-	.63	6.61	.095	2.50	.07	.0009
	LBD	9:00	6.3	53	-	2.56	135.	-	8.90	5.31	41.1	102.							2.92	.13	1.1
	UBD	9:00	7.0	52	-	2.29	136.	-	8.87	11.5	32.0	96.0							3.21	.11	.05
	SCB	8:50	5.9	51	-	2.96	139.	-	9.89	4.27	50.7	107.							2.51	.15	5.3
	DTE	9:15	8.3	46	-	3.08	132.	-	7.30	4.90	24.4	98.6							4.24	.16	.0001
	CLO	9:30	7.8	39	-	2.31	138.	-	6.91	5.19	22.6	111.							3.06	.13	.001
	CLU	9:30	8.8	37	21.5	2.30	132.	4.45	6.59	3.79	19.4	107.	7.82	-	-	.58	6.69	.087	2.91	.13	.00001
	MW	9:30	8.5	27	-	1.00	.41	-	.75	1.51	.10	.0									
	LA	9:30	-	27	9.4	-	-	-	-	-	-	-	12.8								
	MgA	9:30	-	27	49.4	-	-	-	-	-	-	-	-	16.9							
	FB	9:30	-	-	43.2	-	-	-	-	-	-	-									
	SCF	15:40	7.9	49	5.5	1.87	133.	3.63	7.53	-	32.3	97.7	7.78	-	.56	.61	6.60	.092	3.09	.09	.001
	LBD	15:45	6.3	50	-	2.32	136.	-	7.42	-	45.2	102.							2.93	.11	1.3
	UBD	15:50	7.0	50	-	2.14	134.	-	7.38	-	33.7	97.3							3.17	.10	.07
	SCB	15:45	5.9	48	-	2.91	142.	-	7.36	-	56.3	103.							2.80	.14	5.8
8-23	SCF	8:35	7.8	49	6.2	2.74	104.	-	8.42	-	16.6	85.4	7.87	-	-	.65	6.65	.098	3.09	.15	.0009
	LBD	8:35	5.7	53	6.7	5.14	103.	-	7.92	-	29.9	83.1							2.36	.28	5.9
	UBD	8:30	6.4	53	-	3.47	104.	-	8.24	-	21.5	85.5							2.94	.19	.44
	SCB	8:40	5.6	49	-	4.75	105.	-	7.44	-	32.5	89.5							2.05	.27	8.6
	SCF	15:20	7.9	51	-	1.95	110.	-	6.79	-	25.3	79.1							2.99	.09	.0009
	LBD	15:25	6.3	51	-	3.27	111.	-	7.17	-	36.1	84.8							3.83	.16	1.1
8-24	SCF	8:25	7.2	52	6.5	9.62	98.4	-	7.26	-	6.20	96.0	7.84	-	-	.79	6.79	.116	3.74	.64	.004
	LBD	8:33	5.2	51	-	17.4	98.5	-	7.43	-	21.9	99.4							2.23	1.12	15.
	UBD	8:29	5.5	51	-	14.4	95.7	-	7.06	-	15.6	95.6							2.52	.95	5.1
	SCB	8:32	4.8	49	-	15.1	103.	-	8.76	-	18.9	105.							.66	1.03	40.

The effect of magnesium concentration on the operation of the system at reduced hold tank volumes is also interesting. The system appeared to approach inoperable conditions as the magnesium content was decreased to 90-100 mmole/liter. This same result was obtained during Phase III. However, on August 20, supersaturated conditions with respect to gypsum were observed, even at a magnesium content of 120 mmole/liter. On that day, the solid sulfate/total sulfur fraction was 0.15 and the gypsum relative saturation rose to 1.59 on the lower bed. As magnesium was added to reestablish operable conditions, the system returned to subsaturated conditions at 140 mmole/liter of magnesium. Magnesium concentrations were reduced subsequently, but supersaturated conditions in the scrubber were not encountered until the magnesium level dropped below 100 mmole/liter at the end of the test.

4.0 DISCUSSION OF RESULTS

During Phase IV, two separate tests were conducted: 1) elimination of the draft tube effect and 2) reduction of the hold tank volume. The impact of the draft tube elimination on system operation is discussed in Section 4.1. The effects of the reduced hold tank volume are discussed in Section 4.2.

Material balance calculations for the Phase IV test period (see Tables 4-1 and 4-2) indicate that some unsteady-state conditions were encountered. Independent measures of the amount of sulfur removed in the scrubbing system include the gas phase SO_2 depletion ($\Delta SO_2(g)$), the sulfur sorption measured from liquid phase data, and total sulfur exiting the system. At steady-state these values should all be equal. Likewise, the calcium added to and the calcium purged from the system should agree. Some fairly large deviations are noted on some days; however, these differences fall within ranges which might be expected considering that unsteady state conditions had to be dealt with and that the material balance data shown in Tables 4-1 and 4-2 involve as many as seven different entering and exit streams.

One result which is obvious is that a significant amount of sulfate is exiting as soluble sulfate in the liquor. Generally, between 1/3 and 1/2 of the total sulfate exiting the system was in the liquid phase.

The exit rate of soluble sulfate from the system is a direct function of the total liquid blowdown rate. Since the clarifier overflow blowdown stream represented roughly half of the total liquid leaving the system, operation in a closed loop mode would probably have affected system operation somewhat. However, the trends reported concerning the effect of magnesium

TABLE 4-1. DRAFT TUBE ELIMINATION MATERIAL BALANCE RESULTS (gmole/min)[1]

Date	ΔSO_2(g)	ΔS(liq)	ΔCa(liq)	Sulfur sorption (liq)	Ca add rate	Ca solid out	Lime[2] utili-zation	Sulfur solid out	Sulfur[3] liq out	Total sulfur out	Solid sulfate out	Liquid[3] sulfate out	Total sulfate out	Total Oxidation fraction	Solid sulfate/ total sulfur ratio
7-25	383	453	1	452	475	376	.87	326	19	345	16	11	27	.078	.049
7-26	404	306	2	304	520	439	.86	379	19	398	17	11	28	.070	.045
7-27	-	391	2	389	424	474	.86	407	19	426	20	11	31	.073	.049
7-28	-	315	4	312	398	347	.85	296	17	313	22	11	33	.105	.074
7-29	383[4]	559	-2	561	385	355	.85	300	19	319	19	10	29	.091	.064
8-1	330	405	14	393	441	234	.91	214	18	232	12	13	25	.108	.055
8-8 AM	243	550	182	386	298	338	.90	304	11	315	28	11	39	.124	.091
PM	-	372	141	245	298	323	.90	292	15	307	28	12	40	.130	.096

---

[1] Calculational procedures are presented in Appendix F

[2] Lime Utilization = sulfur solid out/Ca solid out

[3] Liquor exiting the system averaged 154 ℓpm (including blowdown and liquor in filter cake)

[4] Estimated from DuPont readings

TABLE 4-2. REDUCED RESIDENCE TIME MATERIAL BALANCE RESULTS (gmole/min)[1]

Date	$\Delta SO_2(g)$	ΔS(liq)	ΔCa(liq)	Sulfur sorption (liq)	Ca add rate	Ca solid out	Lime utili-zation[2]	Sulfur solid out	Sulfur liq out	Total sulfur out[3]	Solid sulfate out	Liquid sulfate out	Total sulfate out	Total Oxidation fraction	Solid sulfate/ total sulfur ratio
8-16	281[4]	403	-5	407	402	201	.87	174	14	188	7.0	5	12	.064	.04
8-17	282	262	192	90	356	389	.89	345	15	360	34	14	48	.133	.10
8-18	254[4]	370	96	286	290	359	.87	311	15	326	29	13	42	.129	.09
8-19	288[4]	488	98	400	311	331	.89	295	19	314	40	16	56	.178	.12
8-22	304	342	24	320	385	352	.86	303	18	321	34	15	49	.153	.095
8-23	280[4]	258	45	217	367	387	.84	324	11	335	38	13	51	.152	.098
8-24	254[4]	401	162	263	277	407	.86	349	19	368	47	15	63	.171	.116

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[1] Calculational procedures are presented in Appendix F

[2] Lime Utilization - sulfur solid out/Ca solid out

[3] Liquor exiting the system averaged 154 ℓpm (including blowdown and filter cake)

[4] Estimated from DuPont readings

on system operation should still be valid, though the specific levels required for successful operation of the Paddy's Run would probably have been altered if closed loop operation had been attained.

4.1 Draft Tube Elimination

The draft tube effect was eliminated by relocating the lime additive point from the draft tube to the main reaction tank. During the initial phases of this run the magnesium content was maintained between 130 and 140 mmole/liter. Generally, the results were similar to those noted in Phase III. The SO_2 removal efficiency remained above 99 percent, and as can be seen from Table 4-1, the amount of calcium solids dissolving on the bed was minimal. The oxidation fractions and gypsum relative saturations experienced were also about the same as in Phase III.

Beginning August 1, the magnesium concentration was decreased. The trends here were also similar to those in Phase III. The SO_2 removal decreased, calcium dissolution in the scrubber increased, and the oxidation fractions and gypsum relative saturations increased.

One significant difference noticed during this test was the level of magnesium required for system operability. The system remained operable with magnesium concentrations in the 80 to 90 mmole/liter region, and approached inoperable limits only when the magnesium content dropped into the 75 millimolar range. However, it is possible that high liquid blowdown rates during the latter part of the draft tube elimination testing accounted for this behavior although this was not documented quantitatively. The scrubber system operators reported adding water to the reaction tank, but the amounts were not recorded.

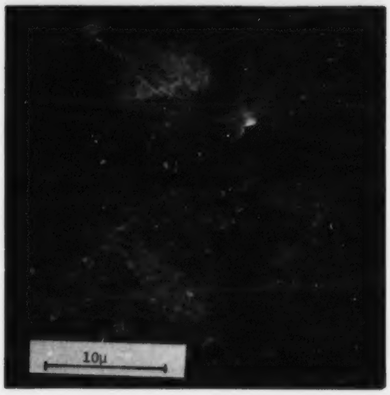
Increased blowdown could, at least partially, explain the successful operation of the system at lower magnesium levels than those needed in Phase III.

The major effect expected from the lime additive point change was a change in solid crystal structure. As explained in Section 2.0, the addition of lime in the hold tank should reduce the driving forces for nucleation and therefore should increase the average particle size.

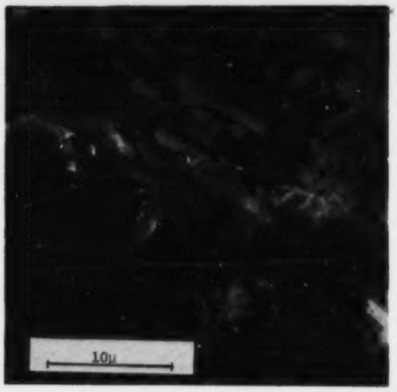
The location of the calcium sulfite precipitation changed as expected. Calculations based on the data gathered on August 1 indicate that of the 449 gmole/minute $CaSO_3$ solids precipitating in the hold tank system only 116 gmole/minute was occurring in the draft tube (due to backmixing). Thus, the majority of the precipitation was occurring in the main reaction tank and surge tank. However, rate calculations cannot determine the dominant precipitation mechanism. Precipitation in the main reaction tank may still have been due to localized nucleation.

A series of electronmicrographs taken during the test reflect apparent changes in the crystal morphology. These micrographs are presented in Figures 4-1 and 4-2. Differences in crystal structure appear to have resulted from both the lime additive change and the reduction in magnesium concentration.

Comparison of the July 26 and July 30 solids reveals a basic change in the crystal structure. The solids in the system on July 26 are mainly rosettes. On July 30 the crystals are somewhat larger, more platelet-like, and the individual crystals are less aggregated. It is reasonable to expect that some change in system operation is responsible for this effect.



JULY 26



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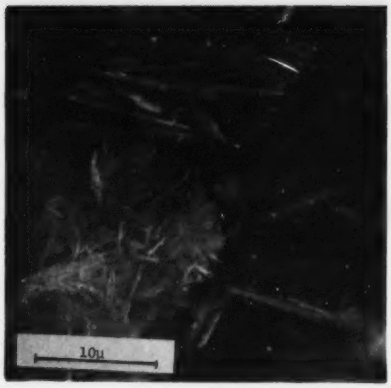
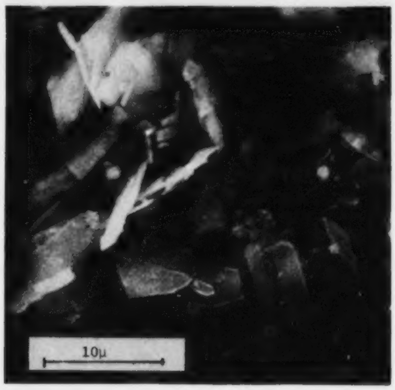


AUGUST 2



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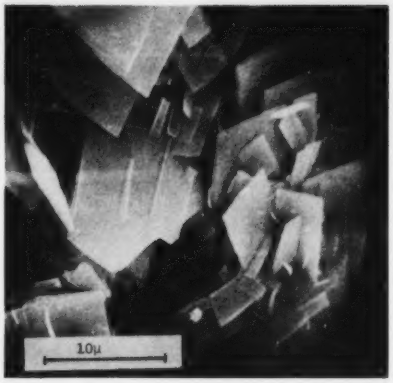
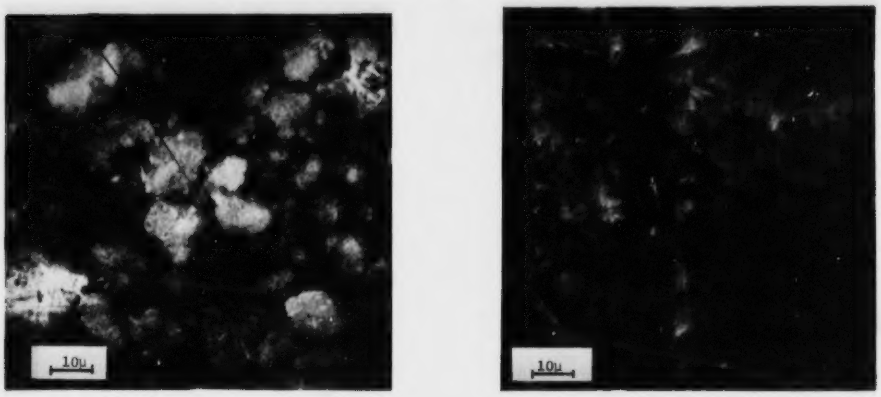


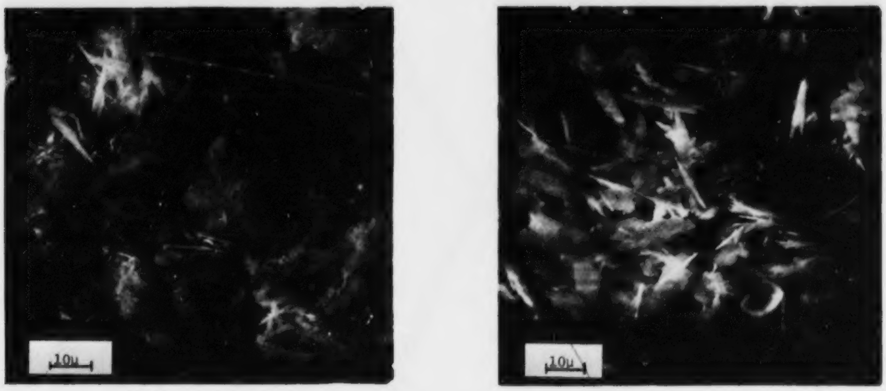
AUGUST 8

FIGURE 4-1 ELECTRON MICROGRAPHS FOR DRAFT TUBE ELIMINATION TEST



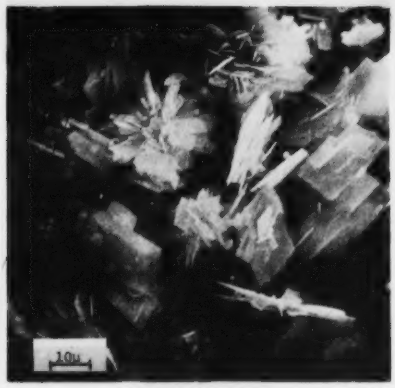
JULY 26

JULY 30



AUGUST 2

AUGUST 4



AUGUST 8

FIGURE A-2 ELECTRON MICROGRAPHS FOR DRAFT TUBE ELIMINATION TEST

In order to properly account for the process factors which might influence the characteristics of the product solids, the conditions which prevailed prior to the time that the product solids were sampled must be examined. The solid phase residence time in the scrubbing loop during the reduced hold tank volume test period was on the order of one day. Since the lime additive point was not changed until mid-day on July 25, the July 26 solids were mainly an artifact of the Phase III operation. During the July 22-26 time period the lime addition point was in the draft tube, and the magnesium concentration was between 130 and 140 mmole/liter. The main difference in the operation of the scrubbing system was the relocation of the lime addition point.

From the preceding discussion, it appears that the lime additive point change did impact the precipitation mechanism in some manner. In theory, this change should tend to reduce the amount of nucleation and lead to more orderly crystal growth. As shown in Figures 4-1 and 4-2, the particles do appear to have increased in size between July 26 and July 30. Platelet formation is one expected result of more orderly crystal growth and less nucleation.

Another significant operating variable change which was seen during this period was in the amount of SO_2 being sorbed. The highest inlet gas SO_2 concentrations seen during the program were measured between July 25 and July 30. This led to higher than average SO_2 sorption rates and an increase in soluble sulfite (which would tend to promote nucleation in the hold tank). So, while the lime additive point change tended to reduce the nucleation rate, the increased SO_2 removal rate tended to counteract this effect.

The magnesium concentration was reduced beginning August 1. By August 2, the magnesium level had dropped to 117 (from 133) mmole/liter. Small differences are discernible between the July 30 and August 2 solids. Less aggregates are seen and the crystals appear to be better defined. Further reduction to about 94 mmole/liter magnesium was accomplished by August 4. Although sufficient time for solid phase line-out was not provided, the solids sampled on August 4 appear to be more platelet-like and slightly larger. On August 8, after several days of operation at magnesium concentrations below 100 mmoles per liter, the solid crystals were larger with a significant number of platelets present although some aggregates are apparent.

The solid crystals from August 8 show significant platelet structure similar to that typically seen in limestone systems. It appears that the lime additive point change in conjunction with a reduction in the magnesium concentration significantly influenced the product crystal structure. However, due to limits on operating time, these effects could not be separated.

As mentioned in Section 3.1, a solid-liquid separation problem in the clarifier led to a recirculating solids control problem beginning on August 1 and lasting until August 7. It is possible that the characteristics of the solids generated during this period caused the problem. As the solids underwent the transition from small rosettes to larger platelets and aggregates, intermediate sized platelets and dendrites were formed. These solids may not settle as well as either rosettes or platelets. This, in turn, could have reduced the clarifier efficiency.

The results of settling rate experiments are consistent with the problems observed in the clarifier. The results from these solids settling experiments are shown in Figure 4-3. Solids sampled on July 25, 26, 27, and August 1 settled much better than those sampled on August 1 and 4 when the clarifier problems existed. These periods of poor settling correspond to the period when the transition solids noted above were present.

Superimposed on the clarifier settling problems was a possible flocculant addition problem. The flocculant addition system was unreliable and may have contributed to the clarifier's inefficiency. However, the flocculant addition problems should not have caused the initial change in solid crystal structure.

4.2 Reduced Hold Tank Volume

During the period between August 8 and 16, the main reaction tank was eliminated from the scrubbing loop. From the standpoint of operation in this mode, two general problems were encountered, but neither of them was severe. First, the pH control was somewhat sensitive to system changes. With the pH sensor in the overflow line between the draft tube and the surge tank, some fairly large pH fluctuations were observed. The draft tube residence time was approximately 20 to 30 seconds, and the response time of the controller became significant when compared to the lime dissolution time and transient changes in SO_2 sorption. Moving the pH sensor into the surge tank helped to alleviate this problem, but pH fluctuations larger than normal did occur throughout the short residence time test.

A second problem encountered was one of liquid level control in the scrubbing loop. Normally, the mist eliminators were washed once per shift at Paddy's Run. The amount of liquid

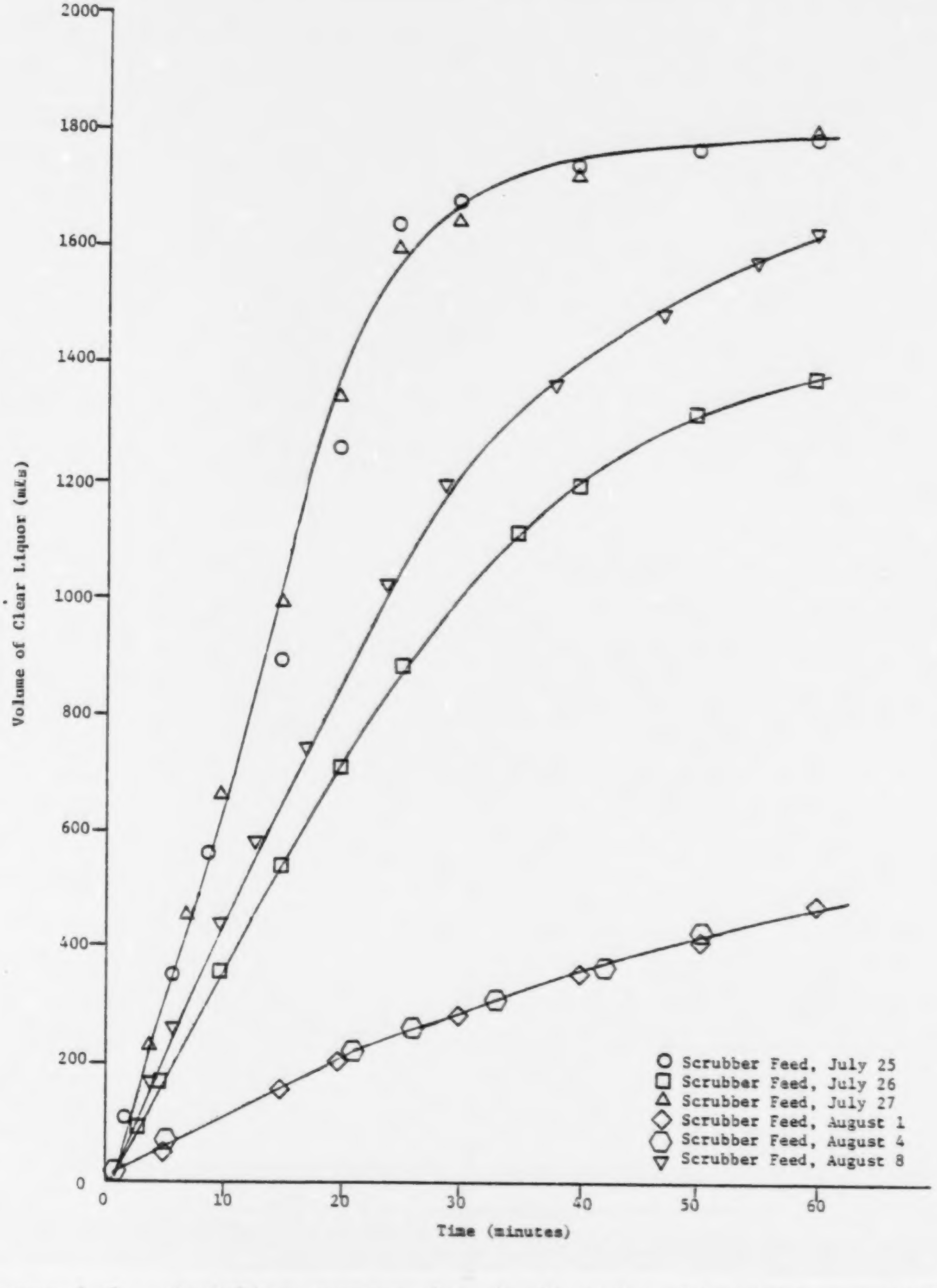


Figure 4-3. Settling curves for draft tube elimination solids (all 3 percent slurries).

added to the system as a result of this operation was about 9100 liters. This resulted in an increase in the surge tank liquid level of about 0.6 meters. To dampen liquid level fluctuations, the upper and lower mist eliminators were washed at separate times. Although more attention to liquid level was necessary, no major difficulties occurred. Basically, operation went smoothly even during start-up.

The process chemistry of the system appeared to have changed slightly during the reduced reaction volume test. As was common during all magnesium testing, higher magnesium concentrations tended to give higher SO_2 removals and lower oxidation fractions. However, during the reduced reaction time test, the oxidation fractions were somewhat higher than those experienced in other tests at equivalent magnesium concentrations. Solid phase sulfate/total sulfur ratios for operation in the 130-140 mmole per liter magnesium range in both the normal configuration and the no draft tube configuration were between 0.04 and 0.07. Similar operation in the reduced residence time configuration resulted in a solid sulfate/total sulfur ratio of above 0.09. While this change clearly has an obvious impact on system operation, the mechanism by which the reduction in residence time caused this change cannot be determined conclusively from the data gathered.

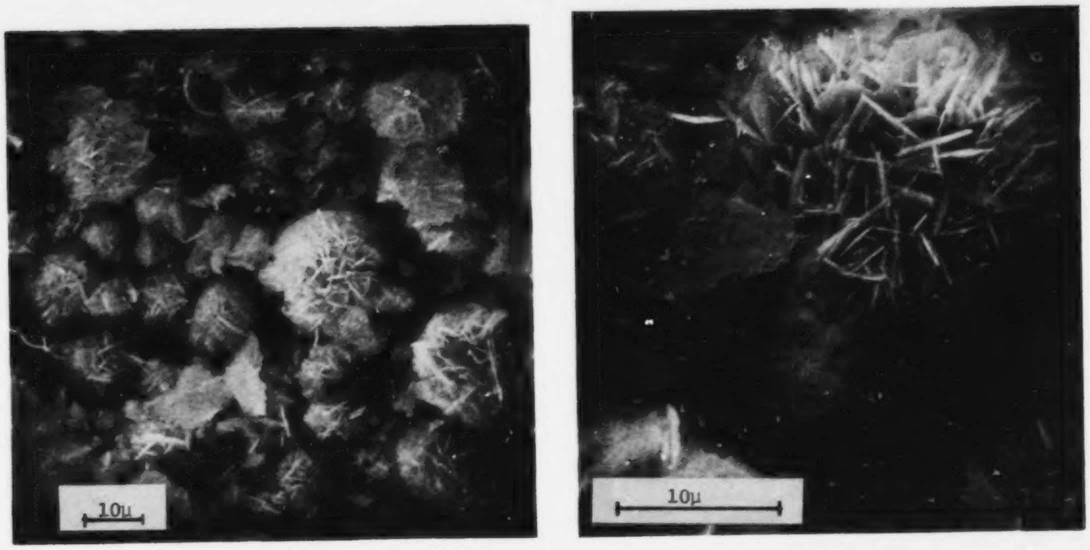
One operating condition which may have contributed to the increased oxidation was the fluctuation in the system's liquor levels. Due to the reduced system volume, control of the tank liquor level was more critical. Generally, the average surge tank level was somewhat lower than its normal value during previous operation. With the bottom of the draft tube sealed and the lower liquid levels, the mixing efficiency of the draft tube agitator was increased. At times, the top agitator blade was exposed which created a frothing effect. This should have increased oxygen transfer and may have influenced the oxidation rate.

The system's response time was also less in the reduced volume configuration. The solid phase residence time had been cut by a factor of four so fluctuations in system operation were more noticeable. Effects which may have been damped out during previous operation were more apparent.

The sensitivity of the system to changes seems to be highlighted by an occurrence on August 20. At a magnesium concentration of about 120 mmole/liter, the solid sulfate/total sulfur rose to 0.15. A gypsum relative saturation of 1.59 was calculated for the lower bed liquor. Magnesium addition to a level of above 140 mmole/liter eliminated the scaling condition. However, subsequent reduction in the magnesium level below 120 mmole/liter did not yield such a sharp increase in the oxidation rate. In fact, the system remained operable down to a magnesium level of approximately 100 mmole/liter. The system appears to have gone through a brief period of high oxidation on August 20 which emphasizes the sensitivity of the system to process upsets during the reduced hold tank volume test.

Operation in the reduced hold tank residence time configuration confirmed that nucleation with rapid precipitation on crystal surfaces is the primary precipitation mechanism when the lime is added to the draft tube. A material balance around the draft tube for August 22 operation shows that virtually all of the 348 gmoles per minute of sulfur precipitation occurs in the draft tube. Since the vessel is relatively small (volume 12,500 liters) most of this precipitation is a direct result of formation of small nuclei and growth on those nuclei.

During the reduced residence time test, no solids control problems were encountered. Figure 4-4 shows electron micrographs from this period. As can be seen in the figure, the solids were mostly rosettes. A settling curve for the August 22 scrubber feed solids is presented in Figure 4-5. This settling rate curve is similar to those obtained in the periods where the clarifier functioned normally during Phase III and during Phase IV with no draft tube.



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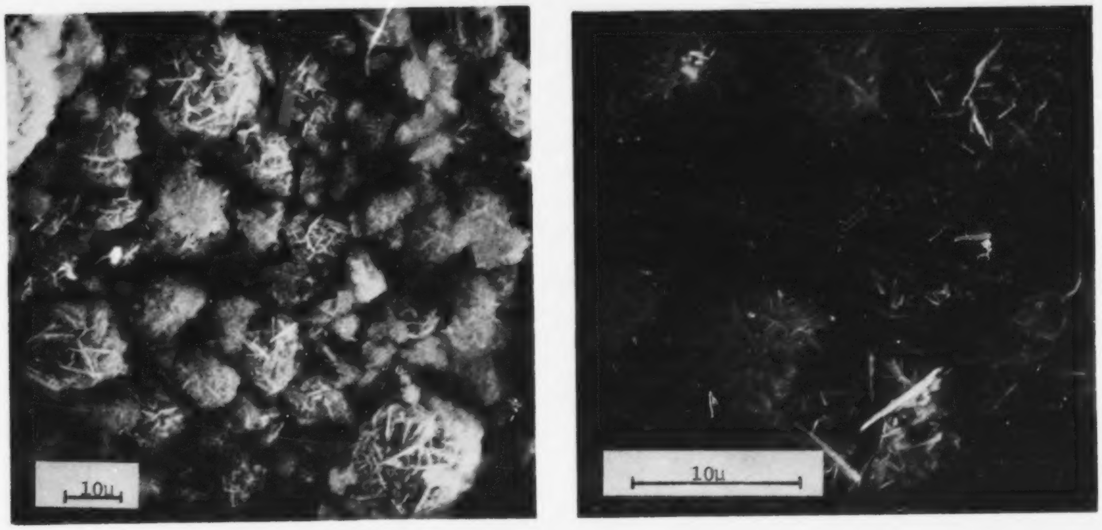

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FIGURE 4-4 ELECTRON MICROGRAPHS FOR SOLIDS FROM REDUCED RESIDENCE TIME TEST

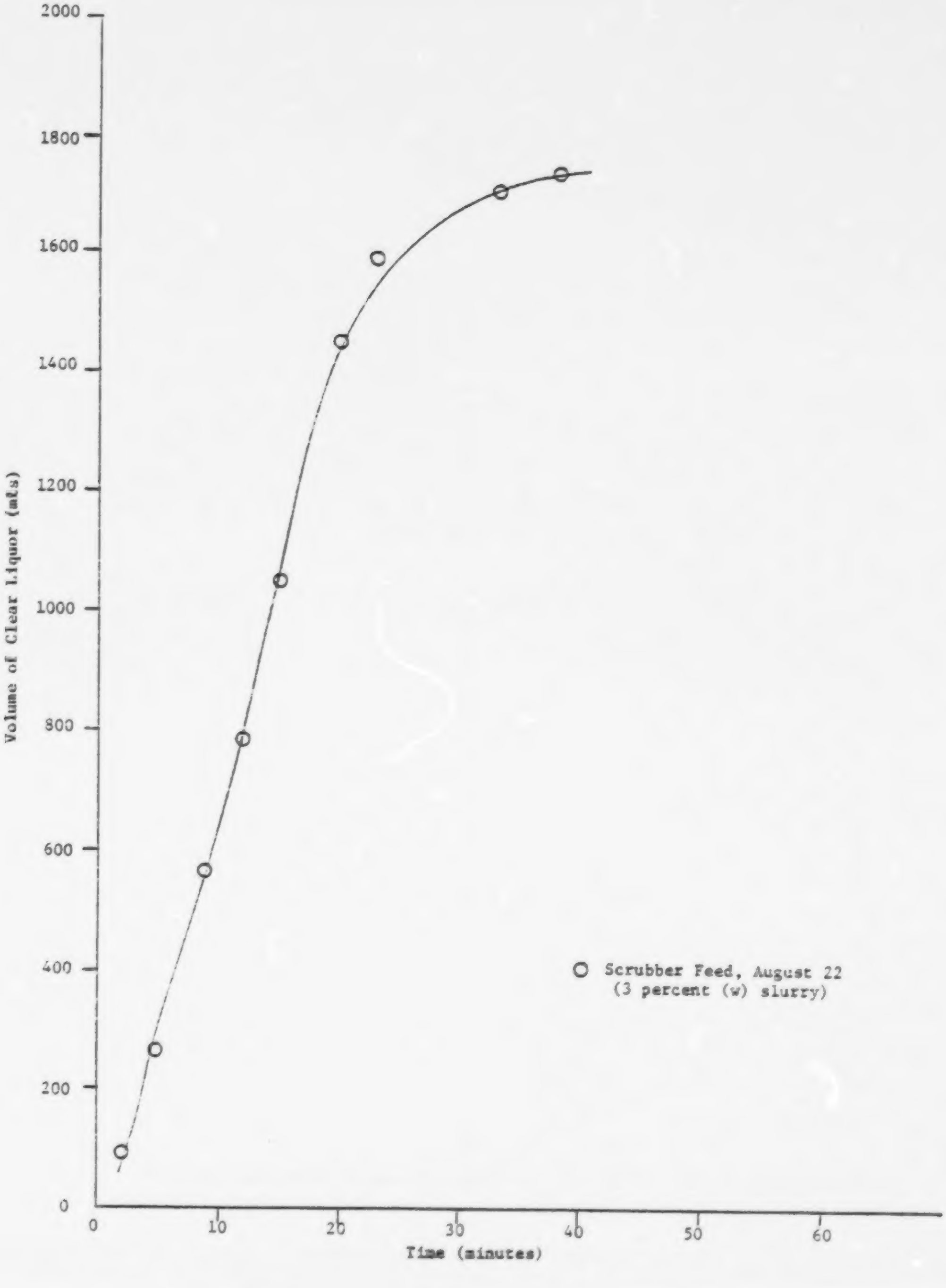

Figure 4-5. Solid settling curve for reduced residence time test.

APPENDIX E

PHASE V
CHLORIDE ADDITION

1.0 SUMMARY

Testing in Phase V simulated conditions which would have existed when burning a high chloride coal at Paddy's Run. By adding $CaCl_2$ to the scrubbing liquor, soluble chloride levels were increased and the resulting impact of this change on system operation was observed.

The Phase V results indicate that increases in soluble chloride levels reduce the liquid phase alkalinity of the scrubbing slurry, and that increases in the magnesium concentration can offset this effect. In the Paddy's Run system, with a magnesium concentration of 150 mmole/liter, an initial 270 mmole/liter (9600 ppm) spike in chloride concentration led to scaling conditions in the scrubber and a reduction in SO_2 removal efficiency from about 98 percent to 90 percent. A subsequent decrease in chloride to 80 mmole/liter, accompanied by an increase in magnesium to about 160 mmole/liter, restored 98 percent SO_2 removal efficiency and led to conditions which were subsaturated with respect to gypsum throughout the system. The magnesium level was increased from 125 mmole/liter, which maintained system operability at the end of Phase IV, to 160 mmole/liter in order to compensate for the 70 mmole/liter increase in steady-state chloride concentration. This increase was one mole of Mg^{++} per two moles of Cl^- added. Thus, an increase in chloride has been shown to decrease liquid alkalinity while increases in magnesium concentration were shown to offset this reduction. This result is valid at least in the ranges of Cl^- and Mg^{++} investigated in this program.

The decrease in liquid alkalinity which results from chloride increases can be explained by considering ion balances. As the chloride ion concentration increases, the calcium concentration (when magnesium and sodium concentrations are held constant) must increase to maintain an electrically neutral solution. This increase in calcium will decrease the amounts of sulfite, carbonate, and sulfate which can remain in solution since these calcium salts are fairly insoluble. Thus, the chloride ion displaces less soluble, more alkaline species such as sulfite and carbonate.

The effect of increasing magnesium is to offset the loss of alkalinity due to chloride increases. Since the magnesium salts are more soluble than the calcium salts, addition of one mole of Mg^{++} for every two moles of Cl^- in solution will satisfy electrical neutrality requirements without causing an increase in the calcium ion concentration. Thus, an appropriate amount of magnesium addition can balance a chloride concentration increase and maintain the system's liquid phase alkalinity.

2.0 TEST APPROACH

Phase V was designed to test the effect of higher liquid phase chloride concentrations on scrubber system operation. Normally, during combustion, chloride in the coal forms hydrochloric acid which is then absorbed from the flue gas by the alkaline FGD scrubbing liquor. The chloride ion is a highly soluble species relative to the other major anions found in the scrubbing liquor. Thus, the liquid phase chloride concentration will increase until the chloride sorption rate from the gas to the liquid is equal to the liquid phase chloride purge rate from the system. The coal burned at Paddy's Run typically had a low chloride concentration. Combustion of a higher chloride coal was simulated by the addition of $CaCl_2$ to the scrubbing liquor.

The addition of $CaCl_2$ to the system was conducted in conjunction with increases in magnesium concentration. Originally, the chloride level was to be increased until the system approached scaling conditions. Then magnesium was to be added to reestablish subsaturated conditions. Since the system had been inoperable without magnesium addition in Phase II and sufficient time for separate chloride and magnesium tests was not available, the $CaCl_2$ addition test was conducted at a magnesium concentration which was already fairly high. The magnesium was added to offset the reduction in liquid phase alkalinity which was expected to accompany the increase in chloride level.

Phase V testing was conducted with the reduced hold tank volume configuration which was employed in Phase IV. A schematic flow diagram which shows this configuration is provided in Figure 2-1. In this configuration, the solids residence time was about 4 to 5 hours.

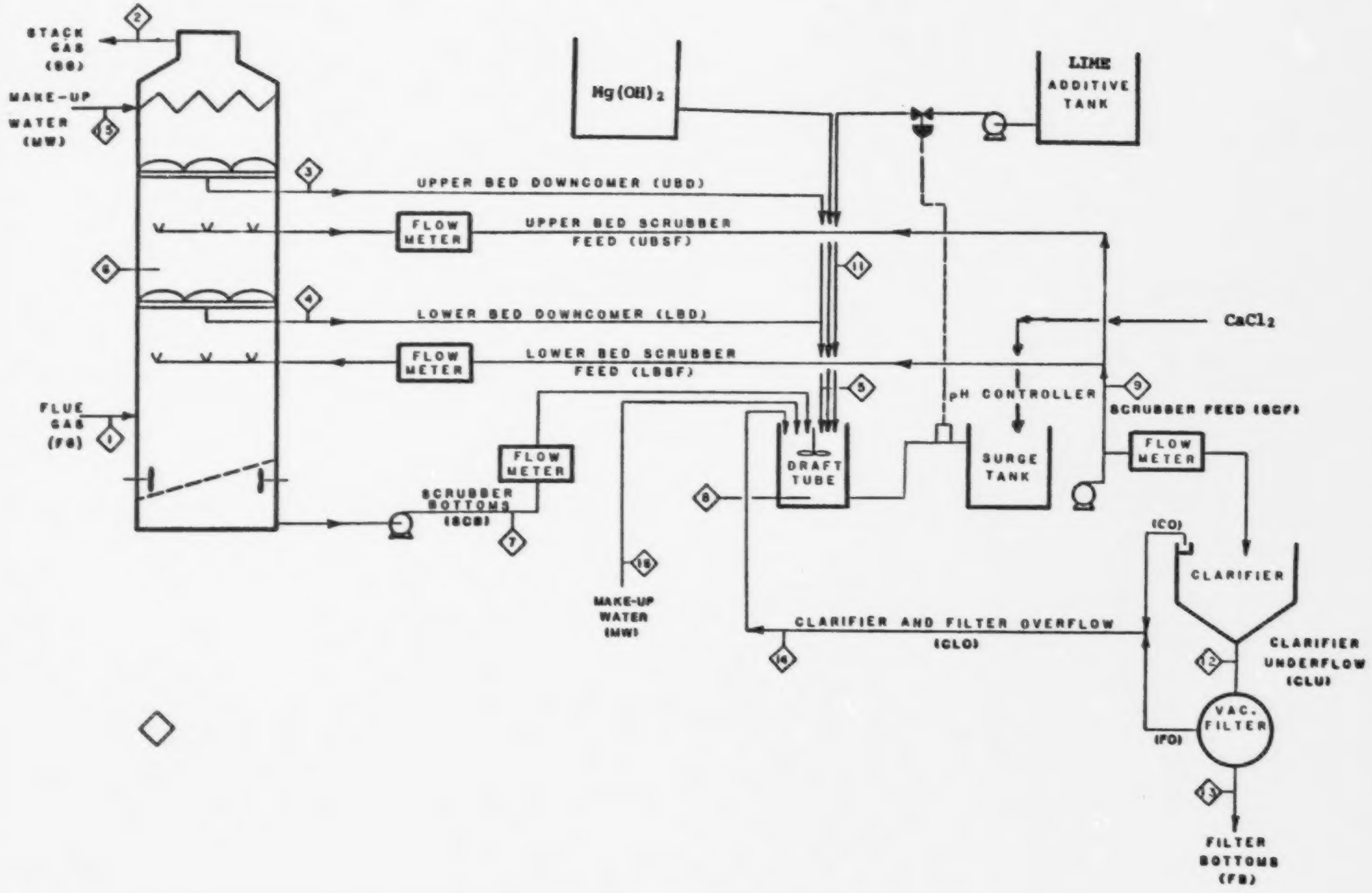
STACK GAS (SG)
2
MAKE-UP WATER (MW)
15
Mg(OH)₂
LIME ADDITIVE TANK
3
UPPER BED DOWNCOMER (UBD)
FLOW METER
UPPER BED SCRUBBER FEED (UBSF)
6
11
4
LOWER BED DOWNCOMER (LBD)
CaCl₂
FLOW METER
LOWER BED SCRUBBER FEED (LBSF)
5
pH CONTROLLER
9
SCRUBBER FEED (SCF)
FLUE GAS (FG)
1
FLOW METER
DRAFT TUBE
SURGE TANK
FLOW METER
8
SCRUBBER BOTTOMS (SCB)
7
(CO)
CLARIFIER
18
MAKE-UP WATER (MW)
CLARIFIER AND FILTER OVERFLOW (CLO)
16
12
CLARIFIER UNDERFLOW (CLU)
VAC. FILTER
(FO)
13
FILTER BOTTOMS (FB)

Figure 2-1. System configuration for Phase V Testing (Flow Scheme III - five minute residence time).

3.0 RESULTS

The process and analytical results generated during Phase V, which lasted from August 24 to August 31, 1977, are reported in this section. Important operating parameters are summarized in Figure 3-1. In addition, detailed process measurements are provided in Table 3-1 and the analytical data gathered is presented in Table 3-2.

On August 24, an initial charge of $CaCl_2$ solids was added to the reaction surge tank. Sufficient $CaCl_2$ was added to increase the chloride ion concentration to about 80 mmole/liter (2800 ppm) in both the clarifier and scrubbing loop liquors. Since several hours were required for the chloride concentration in the clarifier to approach the desired level, the initial chloride concentration in the scrubbing loop exceeded 270 mmoles/liter (9600 ppm).

The initial chloride charge on August 24 resulted in several system changes. From Table 3-2, it is seen that the soluble calcium concentration had increased by about ten-fold relative to previous and subsequent operation. Significant calcium dissolution was also occurring across the lower bed. This is indicative of lower liquid phase alkalinity levels. The gypsum relative saturation was 1.01 in the scrubber feed stream and 1.42 in the lower bed downcomer streams. These results indicate that prolonged operation under these conditions would have led to scaling in the scrubber.

Prior to the addition of $CaCl_2$, the magnesium concentration was increased to about 150 mmoles/liter. Eventually a level of 160 mmole/liter of magnesium was attained in the system. About 120 to 130 mmoles/liter of magnesium had

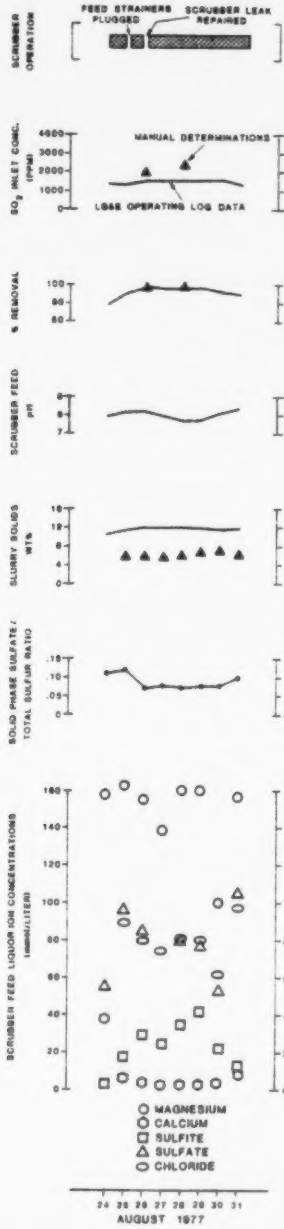

Figure 3-1. Phase V operating summary.

TABLE 3-1. PHASE V - PROCESS MEASUREMENTS
Test Objective: Chloride (and magnesium addition) Testing

	Test #16						Test #17[1]
	Aug. 25	Aug. 26	Aug. 27	Aug. 28	Aug. 29	Aug. 30	Aug. 31
Flue gas (Nm^3/hr) (dry)	-	159,000	162,000	167,000	-	-	-
SO_2 inlet (ppm)	2,120	2,440^2	2,370	2,440^2	2,440^2	2,300^2	2,180^2
SO_2 outlet (ppm)	8	50^2	15	25^2	25^2	30^2	30^2
% Removal	99.6	98.0	99.4	99.0	99.0	98.7	98.6
Scrubber feed (ℓpm)	25,700 →	→	26,100	25,700 →	→	26,100 →	→
Upper bed	12,900 →	→	13,100	12,900 →	→	13,100 →	→
Lower bed	12,800 →	→	13,000	12,800 →	→	13,000 →	→
L/G (ℓ/Nm^3)	-	9.7	9.6	9.2	-	-	-
Slurry solids wt %	6.7	6.5	6.1	6.7	7.0	7.2	6.5
Scrubber feed pH	7.9	7.8	7.7	7.8	7.5	7.1	7.6
Scrubber bottoms (ℓpm)	5,000 →	→	→	→	→	5,150 →	→
Clarifier feed (ℓpm)	541	643	753	738	700	644	651
Clarifier overflow (ℓpm)	-	-	-	-	-	-	473
Lime additive (ℓpm)	253	280	303	273	415	529	122[1]

[1] Carbide lime employed as additive for one day.

[2] SO_2 values from corrected DuPont readings.

Note: The Downcomer flow rates are estimated from C.E. phototype data. Typically, the reject rate from each bed is equal to the scrubber bottoms rate. However, in this case leaking nozzles caused the lower bed reject rate and thus the scrubber bottoms rate to be somewhat higher than the upper bed reject rate.

TABLE 3-2. CHEMICAL DATA SUMMARY

Sample identification				Slurry Properties			Liquid analyses (mmol/liter)							Solid analyses (mmol/g)						Computer results		
Test	Date	Stream[1]	Time	pH	Temp (°C)	% Solids	Ca^{++}	Mg^{++}	Na^{+}	Cl^{-}	$CO_3^{=}$	$SO_3^{=}$	$SO_4^{=}$	Ca^{++}	Mg^{++}	$CO_3^{=}$	$S.SO_4^{=}$	T.S.	Ox Frac	$CaSO_3 \cdot RS$	$CaSO_4 \cdot RS$	$P^{*}SO_2$ (PPM)
16	8-24	SCF	16:00	7.8	51	-	38.1	148.	-	273.	-	3.1	50.8							4.65	1.01	.00006
		LBD	16:00	5.1	51	-	51.4	157.	-	270.	-	18.5	59.8							3.72	1.42	11.
	8-25	SCF	8:30	7.9	51	6.7	4.02	165.	-	89.8	-	18.5	97.1	7.24	-	-	.80	6.42	.125	3.48	.167	.0004
		LBD	8:34	5.8	52	-	6.03	165.	-	93.1	-	32.1	99.1							2.84	.281	3.8
		UBD	8:28	6.3	52	-	4.99	164.	-	93.3	-	20.0	100.							2.84	.203	.42
		SCB	8:35	5.8	48	-	5.04	170.	-	95.3	-	33.9	102.							2.62	.230	4.0
	8-26	SCF	8:25	7.8	52	6.5	2.77	153.	-	80.0	-	29.6	82.6	7.47	-	-	.51	6.61	.077	3.80	.108	.001
		LBD	8:32	6.0	52	-	3.17	154.	-	81.1	-	37.6	90.3							2.37	.137	2.5
		UBD	8:25	6.8	52	-	2.88	157.	-	79.1	-	31.2	89.8							3.01	.120	.10
		SCB	8:30	5.5	49	-	2.82	160.	-	80.1	-	52.3	92.2							1.32	.121	16.
	8-27	SCF	9:25	7.7	53	6.1	2.32	137.	-	75.4	-	25.3	78.6	7.23	-	-	.50	6.34	.079	2.98	.095	.002
		LBD	9:28	6.0	51	-	3.81	137.	-	79.3	-	38.4	81.8							3.12	.160	2.7
		UBD	9:24	6.7	51	-	2.50	138.	-	75.3	-	27.0	78.8							2.80	.103	.14
		SCB	9:30	5.5	50	-	3.40	143.	-	78.0	-	47.3	82.0							1.53	.143	14.
	8-28	SCF	9:18	7.8	53	6.7	1.92	161.	-	82.4	-	35.7	83.1	7.63	-	-	.50	6.72	.074	2.95	.070	.001
		LBD	9:26	6.6	52	-	2.01	159.	-	82.2	-	51.2	83.9							3.20	.070	.40
		UBD	9:23	6.7	52	-	1.91	161.	-	82.9	-	39.2	82.0							2.61	.070	.19
		SCB	9:25	5.1	50	-	2.16	166.	-	86.1	-	61.8	89.0							.52	.087	51.
	8-29	SCF	8:30	7.5	54	7.0	1.76	157.	3.64	80.0	-	43.2	73.6	7.23	-	-	.50	6.45	.078	3.11	.056	.007
		LBD	8:36	6.3	53	-	1.95	161.	-	81.7	-	56.6	77.2							2.71	.064	1.3
		UBD	8:32	6.8	53	-	1.91	161.	-	82.4	-	43.0	78.4							2.89	.065	.14
		SCB	8:35	5.6	51	-	1.95	165.	-	80.8	-	72.3	80.4							1.36	.067	16.
		DTE	8:50	7.9	53	-	1.99	160.	-	78.3	-	41.2	75.7							3.46	.065	.001
		CLO	9:00	7.9	41	-	1.48	170.	-	85.2	-	42.4	87.8							2.82	.052	.001
		CLU	9:00	8.4	40	28.8	1.44	163.	3.95	80.8	-	36.8	84.6	7.20	-	-	.50	6.53	.077	2.59	.052	.00009
		LA	9:00	-	-	7.4	-	-	-	-	-	-	-	12.8						-	-	
		MgA	9:00	-	-	54.8	-	-	-	-	-	-	-	-	16.2					-	-	
		MW	9:00	8.8	28	-	.87	.33	-	.87	-	.09	.72							-	-	
		FB	9:00	-	-	48.7	-	-	-	-	-	-	-							-	-	
	8-30	SCF	8:25	7.1	50	7.2	1.96	106.	-	64.1	-	22.7	52.7	7.54	-	-	.48	6.61	.073	2.69	.068	.025
		LBD	8:30	5.7	50.5	-	3.82	101.	-	62.0	-	36.4	51.4							2.19	.126	7.0
		UBD	8:27	6.4	50.5	-	2.07	107.	-	59.8	-	26.8	53.8							2.31	.074	.51
		SCB	8:30	5.5	48.5	-	2.94	112.	-	61.8	-	43.1	60.4							1.44	.113	14.
		LA	11:30	-	-	5.3																
17	8-31[2]	SCF	8:30	7.6	53	6.5	8.62	155.	3.61	95.2	-	9.83	107.	7.05	-	-	.63	6.42	.098	3.99	.469	.0008
		LBD	8:44	5.5	53	-	11.1	157.	-	97.1	-	22.5	111.							2.22	.602	6.3
		UBD	8:35	6.1	53	-	9.92	159.	-	99.2	-	13.1	111.							2.98	.548	-
		SCB	8:35	5.8	50	-	7.94	158.	-	90.8	-	22.6	111.							2.80	.430	-

[1] **Stream Identification**

SCF - Scrubber Feed
LBD - Lower Bed Downcomer
UBD - Upper Bed Downcomer
SCB - Scrubber Bottoms
DTE - Draft Tube Effluent
CLO - Clarifier Overflow
CLU - Clarifier Underflow
LA - Lime Additive
MgA - Magnesium Additive
MW - Makeup Water
FB - Filter Cake Bottoms

[2] **Carbide lime used as additive**

maintained system operability during the reduced reaction time test in Phase IV. Therefore, a magnesium increase of about 35 mmole/liter above this level was needed to offset the 70 mmole/liter increase in chloride.

With the increase in magnesium and the decrease in the initial spike in chloride concentration, the system operated in a manner similar to previous operation with magnesium addition only. The results listed in Table 3-2 show that the solid sulfate/total sulfur ratio remained below 0.1, and the gypsum relative saturation remained below 0.2 in all streams. The SO_2 removal efficiency remained above 98 percent after the initial decrease to about 90 percent which accompanied the chloride concentration spike.

Throughout Phase V, as was the case during all commercial lime testing, clarifier overflow liquor was periodically routed to the ash pond to control liquid level. This rate averaged about 95 liters/minute through August 29. However, a reduction in the lime additive solids concentration on August 29 caused an increase in the blowdown rate. A blowdown rate of 165 liters/minute was measured on August 30.

This increased liquor purge rate is reflected in the decreased soluble ion concentrations measured on August 30. The magnesium concentration dropped from about 160 to 105 mmole/liter, and the chloride concentration decreased from 80 to 65 mmole/liter between August 29 and 30. Since the commercial lime solids concentration in the additive slurry could not be increased at this time, carbide lime slurry was employed as the alkaline additive during the final day of testing. No blowdown was required during the carbide lime operation, and the magnesium and chloride concentrations increased substantially.

4.0 DISCUSSION OF RESULTS

The material balance results from Phase V indicate that the gas flow determinations were biased on the low end. These results are presented in Table 4-1. Three independent measurements of sulfur sorption rate can be calculated. Sulfur sorption can be determined from the gas phase balance ($\Delta SO_2(g)$), from liquid phase balances (sulfur sorption (liquid) around the scrubber, or by measuring the sulfur exit rate from the system. At steady state conditions, these three measurements should agree. Attempts were made to sample the gas and scrubber liquid streams simultaneously. Under these conditions the gas and liquid results should have agreed. However, Table 4-1 indicates that the $\Delta SO_2(g)$ results were consistently lower, by as much as 40 percent in one case. In a system which is operating at steady state, the sulfur exit rate should also equal the sulfur sorption rate. Although there was a 25 percent difference between the total sulfur exit rate and the liquid sulfur sorption rate on August 26, the sulfur exit rate and the liquid sulfur sorption rate agreed to within 10 percent on the other two days. This indicates that the gas phase values are probably low, possibly due to errors in gas flow rate measurement.

Even though some inconsistencies exist in the sulfur material balances, two trends shown during Phase V are significant. First, it appears that addition of significant amounts of chloride would yield inoperable scrubber conditions in the Paddy's Run system. Second, magnesium addition can offset increases in chloride, at least for chloride concentrations of about 80 mmoles per liter.

TABLE 4-1. PHASE V MATERIAL BALANCE RESULTS (gmoles/min)[1]

Date	ΔSO_2(g)	ΔS (liq)	ΔCa (liq)	Sulfur sorption (liq)	Ca solid in	Ca solid out	Lime utilization[2]	Sulfur solid out	Sulfur liquid out[3]	Total sulfur out	Sulfate solid out	Sulfate liquid out[3]	Total sulfate out	Total sulfate out/total sulfur out	Sulfate solid out/sulfur solid out
8-26	245	408	6	403	357	326	0.89	289	19	308	22	14	36	.117	.077
8-27	288[4]	318	24	297	378	332	0.88	290	17	307	23	13	36	.117	.079
8-28	277	350	2	348	348	394	0.88	347	20	367	26	14	40	.109	.074

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[1] Calculation methods employed are presented in Appendix F

[2] Lime utilization = sulfur solid out/Ca solid out

[3] Average total liquor purge rate of 166 liter/minutes used here

[4] Corrected DuPont SO_2 readings used in calculation

The main effect of an increase in chloride on scrubber chemistry appears to be a decrease in liquid phase alkalinity. The chloride ion is a soluble species in scrubbing liquors. Therefore, as the liquid phase chloride concentration increases (without an increase in the concentration of a soluble ion such as magnesium), the concentration of calcium must also increase to maintain an electrically neutral solution. Since the total amount of calcium, sulfite, sulfate, and carbonate which can remain in solution is constrained by solubility requirements, the concentrations of sulfite, sulfate, and carbonate decrease with increasing calcium concentration. Thus, the effect of increasing the level of chloride in the system is to decrease the concentration of the less soluble, more alkaline species such as carbonate and sulfite.

These effects are confirmed by the results from Phase V. On August 24, the chloride concentration was 273 mmole/liter, and the sulfite concentration was 2.1 mmole/liter in the scrubber feed stream. The resulting SO_2 removal efficiency was about 90 percent, and calcium dissolution on the lower marble bed had created scaling conditions. On August 25, after the chloride concentration had decreased to 90 mmole/liter, the scrubber feed liquor calcium concentration had decreased to 4 from 38 mmole/liter and the sulfite concentration had increased to 18.5 mmole/liter. This increase in liquid phase alkalinity resulted in an SO_2 removal efficiency of above 99 percent and minimal calcium dissolution in the scrubber. These results clearly show that increases in chloride level lead to decreases in liquid phase alkalinity.

The effect of magnesium on liquid phase alkalinity was shown in Phase III. In Phase V, magnesium was added to offset the effect of increased chloride. One mole of magnesium was added for every two moles of chloride added. With this approach, the ion balance was maintained without reducing the liquid phase alkalinity. Since system operability had been achieved at 120 to 130 mmole/liter magnesium during the latter part of Phase IV, concentrations of 160 mmole/liter of magnesium were used to offset an increase in chloride concentration of about 70 mmole/liter. System operability was maintained in this way.

The solids produced from the higher chloride and magnesium environment during Phase V were similar to those observed during the reduced hold tank volume testing in Phase IV. Figure 4-1 presents electron micrographs for the August 29 scrubbing slurry solids. The crystal structure indicates that fairly small rosettes were being produced. These solids settled as well as any measured in the program. A settling curve is presented in Figure 4-2. No clarifier operating problems were encountered during Phase V.

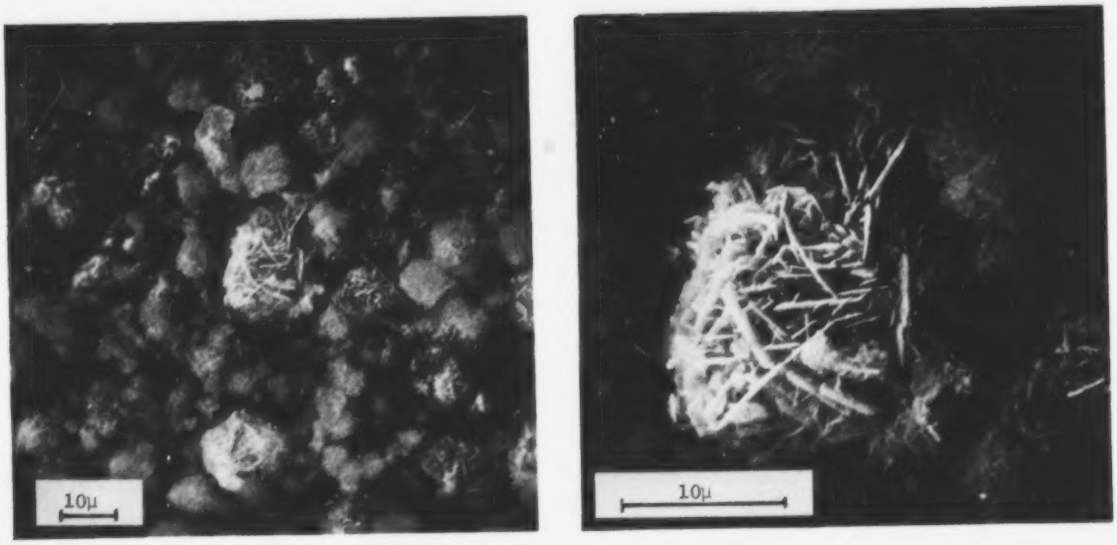

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FIGURE 4-1 ELECTRON MICROGRAPHS FOR PHASE V SCRUBBER FEED SOLIDS

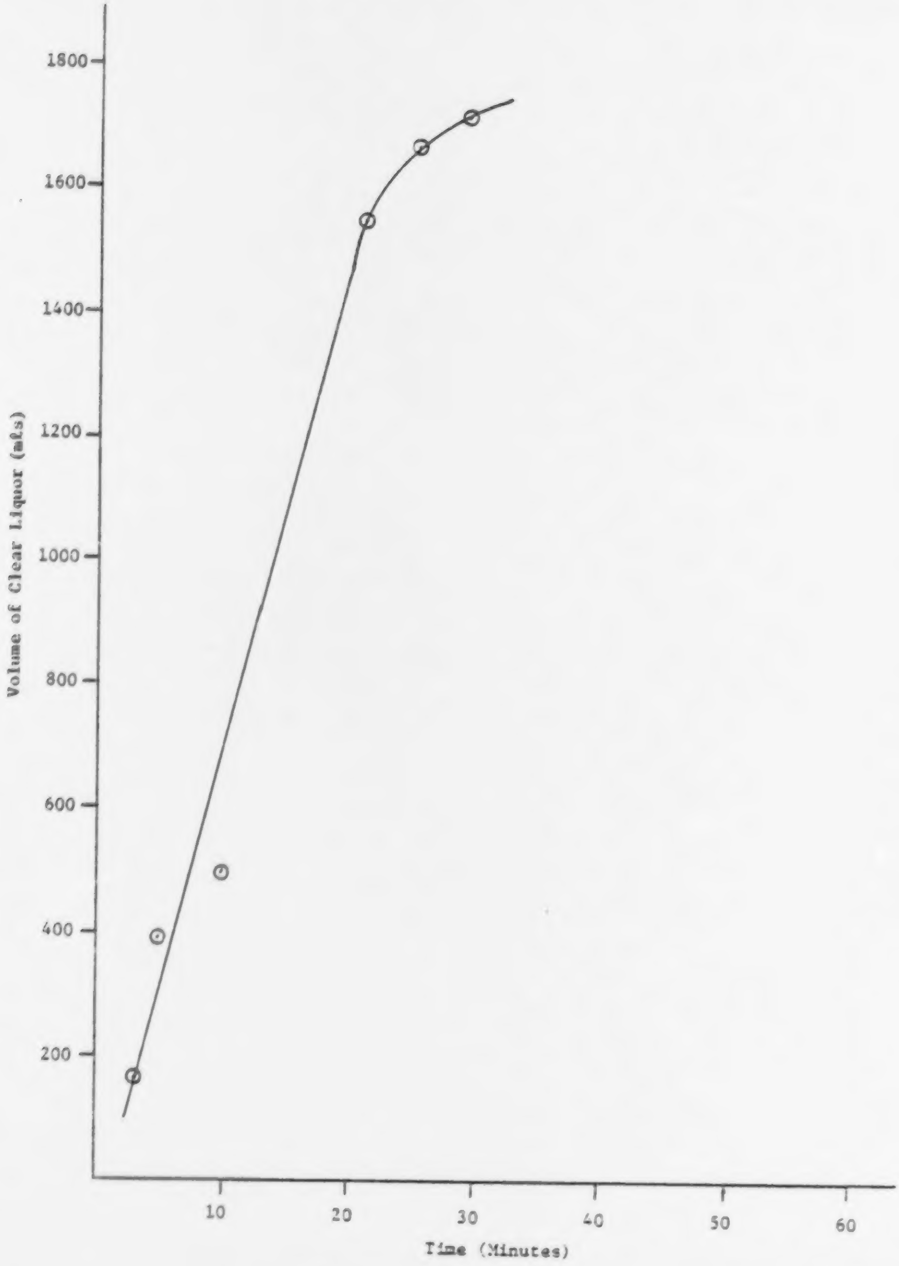

Figure 4-2. Setting curve for Phase V solids.

APPENDIX F

CALCULATIONAL METHODOLOGY

This appendix presents the calculational format used to obtain material balances and rate summaries presented in the previous appendices. Analytical and process data from December 1, 1976 are used in the examples.

Material Balances

Material balances are an accounting of mass flows and changes of mass inventory in a system. As such, they are statements of the law of mass conservation. Based on steady-state operation for the scrubbing system, no changes in the mass inventory occur. Therefore, the material balance is simplified to the following equation.

$$\text{input} = \text{output} \qquad \text{(F-1)}$$

In the calculation of inputs and outputs, analytical and process data are employed. If a reasonable agreement between the values is obtained, it can be assumed that the data used are accurate. If a large difference is found between the input and output values, a discrepancy in at least one of the data is indicated. The analytical and process measurements should be examined to determine the cause of the difference.

Figure F-1 is a simplified scrubbing system which will be used to explain the sulfur balances in the system.

The removal of SO_2 from the flue gas is the objective of this system. A calculation of material balance ① will determine the amount of SO_2 which is removed from the gas phase, $\Delta SO_2(g)$. The second balance ② reflects the amount of SO_2 sorbed into the scrubbing liquor, sulfur sorption (liq). Close agreement between these two values is expected. Calculation of these values requires separate analytical and process data. Therefore, if the results agree, confidence can be placed in the data because it is improbable that compensating errors could occur in both streams and still provide agreement.

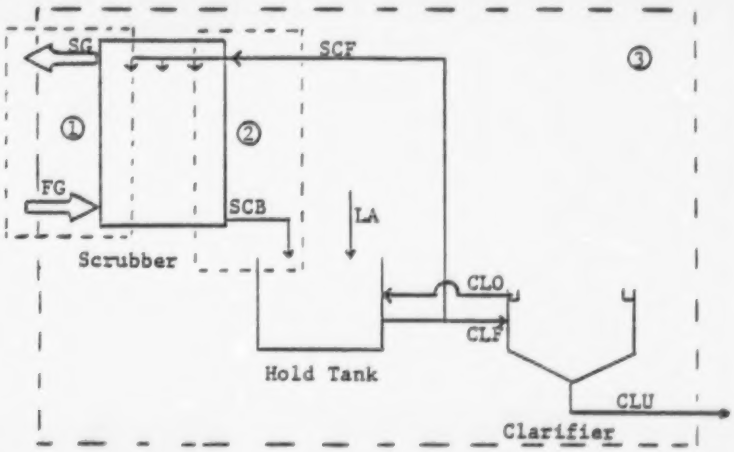

Figure F-1. Simplified scrubbing system.

The third balance, ③ total sulfur out, is directly related to the first two. The SO_2 removed from the flue gas should exactly equal the amount exiting the scrubbing system in a steady-state condition. However, due to the volume involved in the scrubbing loop and the resultant time lag in the processing of the sorbed SO_2, simultaneous sampling of the inlet and outlet sulfur streams often does not generate the same value. Fluctuations in the SO_2 concentration and the flue gas flow rate occur almost instantaneously, whereas these disturbances do not appear in the output for several hours. In addition, the buffering capacity of the large vessels tends to smooth these fluctuations, resulting in an output which is more constant than the output.

Figure F-2 is a diagram of the Paddy's Run scrubber. Stream abbreviations are used in the calculations to represent the stream flow rate.

① The gas phase SO_2 depletion is computed as follows:

$$\Delta SO_2(g) = \text{molar gas flow rate} \quad [SO_2 \text{ concentration in (ppm)} - SO_2 \text{ concentration out (ppm)}] \tag{F-2}$$

$$= \frac{188{,}000 \text{ Nm}^3}{\text{hr}} \; \frac{1 \text{ hr}}{60 \text{ min}} \; \frac{1 \text{ gmole}}{.0224 \text{ Nm}^3} \; (.002370-.000646)$$

$$= 242 \text{ gmole/minute}$$

② The sulfur sorption in the liquid phase involves several calculations. As the scrubbing liquor passes through the scrubber, an increase in the dissolved sulfur concentration is noted. This is calculated as follows:

$$\Delta S(\text{liq}) = \sum_{\text{out}} \text{Total Sulfur(aq)} - \sum_{\text{in}} \text{Total Sulfur(aq)}$$

$$= \text{LBD}(TS_{LBD}) + \text{UBD}(TS_{UBD}) + \text{SCB}(TS_{SCB}) - \text{SCF}(TS_{SCF}) \tag{F-3}$$

$$= \frac{11{,}100 \text{ ℓ}}{\text{min}} \left| \frac{.0304 \text{ gmole}}{\text{ℓ}} \right. + (8000)(.0249) + 3390(.0277) - 22700(.0114)$$

$$\Delta S(\text{liq}) = 372 \text{ gmole/min}$$

Part of this increase in liquid phase sulfur comes from the sorption of SO_2 from the flue gas. However, a significant increase also results from the dissolution of calcium sulfite-sulfate solids. This dissolution is caused by the need for extra alkalinity and has been discussed previously. Since no calcium hydroxide solids were noted by I.R. scan of the scrubber

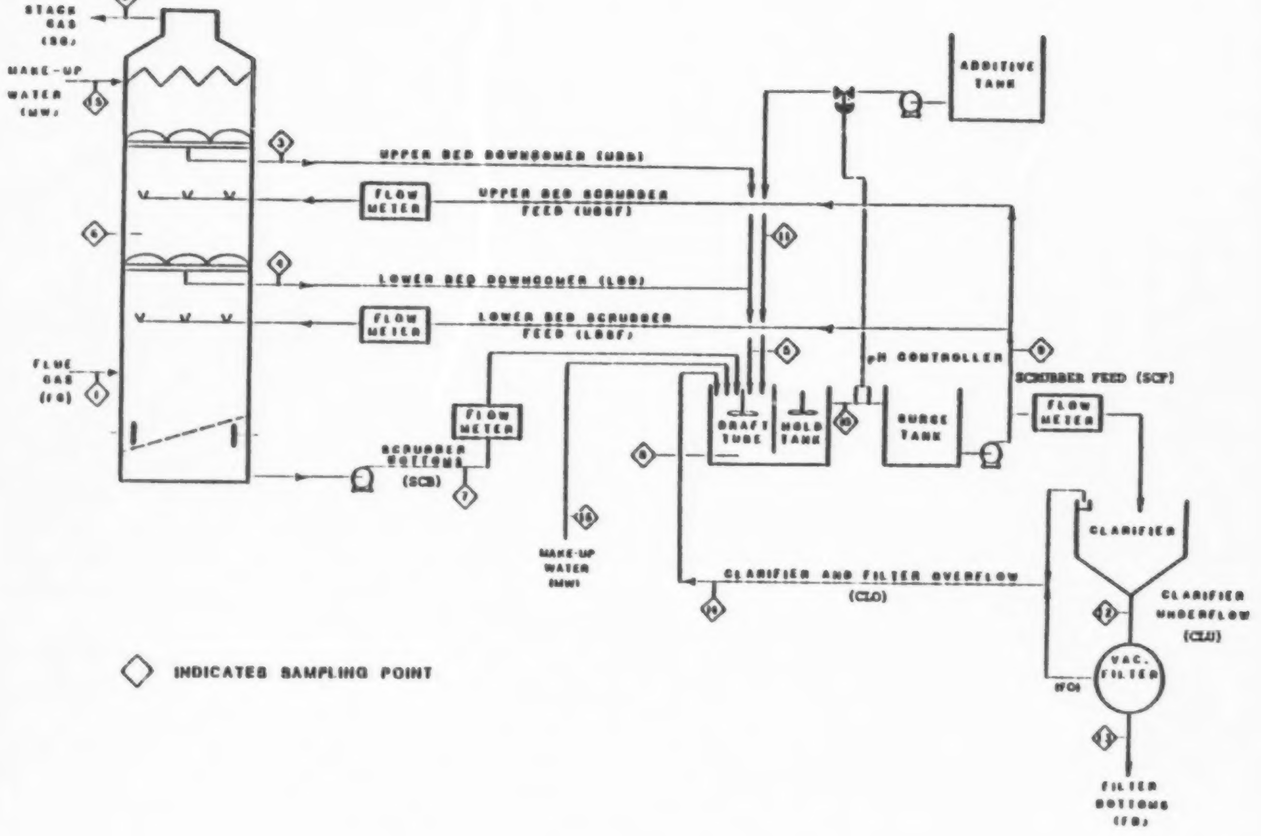
2
STACK GAS (SG)
MAKE-UP WATER (MW)
15
3
UPPER BED DOWNCOMER (UBD)
FLOW METER
UPPER BED SCRUBBER FEED (UBSF)
6
4
LOWER BED DOWNCOMER (LBD)
FLOW METER
LOWER BED SCRUBBER FEED (LBSF)
FLUE GAS (FG)
1
FLOW METER
SCRUBBER BOTTOMS (SCB)
7
16
MAKE-UP WATER (MW)
ADDITIVE TANK
11
5
pH CONTROLLER
9
SCRUBBER FEED (SCF)
8
DRAFT TUBE
HOLD TANK
10
SURGE TANK
FLOW METER
CLARIFIER
CLARIFIER AND FILTER OVERFLOW (CLO)
14
CLARIFIER UNDERFLOW (CLU)
12
VAC. FILTER
(FO)
13
FILTER BOTTOMS (FB)
INDICATES SAMPLING POINT

Figure F-2. Paddy's Run scrubbing system.

feed and all of the calcium carbonate is included in a solid solution with the calcium sulfite-sulfate hemihydrate lattice, the amount of sulfur dissolving is directly proportional to the sulfur/calcium molar ratio in the solids. The rate of sulfur dissolution is then equal to the liquid phase calcium increase times the sulfur/calcium ratio.

The total liquid phase calcium increase[ΔCa(liq)], is computed in the following manner:

$$\begin{aligned} \Delta Ca(liq) &= \sum_{out} Calcium(aq) - \sum_{in} Calcium(aq) \qquad (F\text{-}4) \\ &= LBD(Ca_{LBD}) + UBD\ (Ca_{UBD}) + SCB(Ca_{SCB}) - SCF(Ca_{SCF}) \\ &= 11100(.0263) + 8000(.0235) + 3390(.0249) - 22700(.0177) \\ &= 164 \text{ gmole/minute} \end{aligned}$$

The sulfur/calcium ratio is computed as:

S/Ca = gmoles sulfur per gram of solids/gmoles calcium per gram of solids

$$= \frac{.0066 \ \frac{\text{gmoles S}}{\text{gram}}}{.0073 \ \frac{\text{gmoles Ca}}{\text{gram}}} \qquad (F\text{-}5)$$

$$= .904$$

The liquid phase sulfur sorption can now be calculated using the results from equations F-3, F-4, and F-5.

$$\text{sulfur sorption(liq)} = \Delta S_{liq} - (S/Ca) \cdot \Delta Ca_{liq} \qquad \text{(F-6)}$$

$$= 372 - .904(164)$$

$$= 224 \text{ gmoles/minute}$$

③ The amount of sulfur leaving the system includes the solids in the filter cake and the dissolved species in the liquor blowdown. Calculation of the sulfate leaving in both phases will also be done in order to measure the oxidation rate. The amount of sulfur leaving as a solid can be obtained from the solids analyses and the clarifier feed rate because no solids are returned in the clarifier overflow. This is computed as follows:

$$S_{SOLID\ OUT} = \text{clarifier feed rate} \cdot (\text{weight percent solids}) \cdot (\text{sulfur content}) \cdot (\text{slurry density})$$

$$= \begin{array}{l|l|l|l} 484\ \ell & .0661\ \text{gsolid} & .0066\ \text{gmole} & 1030\ \text{gslurry} \\ \hline \text{minute} & \text{gslurry} & \text{gsolid} & \ell \end{array} \qquad \text{(F-7)}$$

$$= 218 \text{ gmoles/minute}$$

The amount of sulfur leaving as solid sulfate can be computed by using the sulfate to total sulfur ratio in the solids. From the chemical data, the oxidation fraction is obtained as:

$$\text{OxFrac} = \text{sulfate/total sulfur (solid)}$$

$$= \frac{.00066\ \frac{\text{gmoles}}{\text{g}}}{.0066\ \frac{\text{gmoles}}{\text{g}}} \qquad \text{(F-8)}$$

$$= .10$$

Therefore, by multiplying the sulfur solids out by the oxidation fraction, the rate of solid sulfate out is obtained:

$$\begin{aligned}\text{Solid sulfate out} &= 218 \times (.10) \\ &= 22 \text{ gmoles/minute}\end{aligned} \qquad \text{(F-9)}$$

The amount of sulfur leaving in the liquid phase is equal to the blowdown rate times its sulfur concentration plus the filter cake moisture times its sulfur content.

$$\begin{aligned}S_{\text{LIQ OUT}} &= \text{Blowdown rate} \cdot (\text{sulfur level}) + \\ &\quad\ \text{Filter cake moisture} \cdot (\text{sulfur level}) \\ &= 0 + \frac{75\ \ell}{\text{min}} \left| \frac{.0116\ \text{gmole}}{\ell} \right. \qquad \text{(F-10)} \\ &= 0.87 \text{ gmole/minute}\end{aligned}$$

The amount of sulfate leaving in the liquid phase is obtained by multiplying the sulfur liquid out by the sulfate to total sulfur ratio in the corresponding liquid phase.

$$\begin{aligned}\text{Liquid sulfate out} &= 0 + 75(.0115)(.0112/.0115) \\ &= 0.84 \text{ gmole/minute}\end{aligned} \qquad \text{(F-11)}$$

By adding the liquid and solid sulfur and sulfate values one obtains the total sulfur out and the total sulfate out, respectively.

$$\begin{aligned}\text{Total sulfur out} &= 218 + .9 \\ &\simeq 219 \text{ gmoles/minute}\end{aligned} \qquad \text{(F-12)}$$

$$\begin{aligned}\text{Total sulfate out} &= 22 + .8 \\ &\simeq 23 \text{ gmoles/minute}\end{aligned} \qquad \text{(F-13)}$$

Comparison of the three equivalent sulfur balances can now be made. Table F-1 lists these.

TABLE F-1

$\Delta SO_2(g)$ = 242 gmoles/minute
Sulfur Sorption(liq) = 224 gmoles/minute
Total Sulfur Out = 219 gmoles/minute

All of these values agree within about ±10 percent. Since the comparison is based on steady-state values and the size and complexity of the LG&E system makes it unrealistic for a steady-state situation to exist for an extended period of time, these results imply that the data employed in the calculations is reasonably accurate.

Another set of material balances can be used to assess data accuracy. At steady-state, the rate of calcium entering the system should be equal to the rate of calcium exiting the system. Due to the large buffering capacity of the system, changes in one rate are not immediately reflected in the other.

The rate of calcium addition is obtained from the flow rate of the lime additive stream as follows:

$$Ca_{ADD} = \text{lime additive rate} \cdot (\text{weight percent solids}) \cdot (\text{calcium content}) \cdot (\text{additive slurry density})$$

$$= \begin{array}{c|c|c|c} 106\ \ell & .225\ \text{gsolid} & .011\ \text{gmole} & 1100\ \text{gslurry} \\ \hline \text{minute} & \text{gslurry} & \text{gsolid} & \ell \end{array} \tag{F-14}$$

$$= 288\ \text{gmole/minute}$$

The amount of calcium entering in the liquid phase of the lime additive is negligible.

The rate of calcium leaving the system is calculated in the same manner as the total sulfur out.

Ca_{OUT} = clarifier feed rate · (weight percent solids) · (calcium content) · (density)

$$= \frac{484\ \ell}{\text{minute}} \left| \frac{.0661\ \text{gsolid}}{\text{gslurry}} \right| \frac{.0073\ \text{gmole}}{\text{gsolid}} \left| \frac{1030\ \text{gslurry}}{\ell} \right. \qquad \text{(F-15)}$$

= 241 gmole/minute

The amount of calcium leaving in the liquid phase is also negligible.

These two values do not agree within 10 percent. Based on operating knowledge of the system, it is most probable that the lime additive flow rate is not correct.

The final value calculated is the lime utilization. This is the molar ratio of sulfur to calcium in the exiting solids. This value gives an indication of how much of the lime is used for SO_2 scrubbing and how much is precipitated by carbonates and other species.

Lime utilization = total sulfur in the solids/calcium in the solids

$$= \frac{.0066\ \frac{\text{gmoles}}{\text{g}}}{.0073\ \frac{\text{gmoles Ca}}{\text{g}}} \qquad \text{(F-16)}$$

= .90

The amount of calcium entering in the liquid phase of the lime additive is negligible.

The rate of calcium leaving the system is calculated in the same manner as the total sulfur out.

$$Ca_{OUT} = \text{clarifier feed rate} \cdot (\text{weight percent solids}) \cdot (\text{calcium content}) \cdot (\text{density})$$

$$= \begin{array}{c|c|c|c} 484\ \ell & .0661\ \text{gsolid} & .0073\ \text{gmole} & 1030\ \text{gslurry} \\ \hline \text{minute} & \text{gslurry} & \text{gsolid} & \ell \end{array} \qquad \text{(F-15)}$$

$$= 241\ \text{gmole/minute}$$

The amount of calcium leaving in the liquid phase is also negligible.

These two values do not agree within 10 percent. Based on operating knowledge of the system, it is most probable that the lime additive flow rate is not correct.

The final value calculated is the lime utilization. This is the molar ratio of sulfur to calcium in the exiting solids. This value gives an indication of how much of the lime is used for SO_2 scrubbing and how much is precipitated by carbonates and other species.

$$\text{Lime utilization} = \text{total sulfur in the solids/calcium in the solids}$$

$$= \frac{.0066\ \frac{\text{gmoles}}{\text{g}}}{.0073\ \frac{\text{gmoles Ca}}{\text{g}}} \qquad \text{(F-16)}$$

$$= .90$$

Rate Summaries

This section presents the calculations used to obtain mass transfer rates of interest in the LG&E system. The rate calculation summaries indicate the location and the quantity of the solid-liquid mass transfer reactions which occur in the system. This information identifies the relative importance of the different process vessels in relationship to precipitation and dissolution of solids. Again, the data used are from December 1, 1976, and the results obtained have been presented in Table 4-4, Appendix A.

All of the precipitation rate calculations are based on the liquid phase material balances. Solid phase balances cannot be used due to the relatively small amount of solid-liquid mass transfer which occurs when compared to the solid species flow rates. Precipitation and dissolution rates typically are very small relative to the solid species flow rates under consideration. Therefore, mass transfer rates calculated from solid phase data typically involve differences of large numbers and are not as accurate as liquid phase balances.

There are four vessels in the scrubbing loop where precipitation/dissolution can occur. These are the scrubber, draft tube, the main hold tank, and the surge tank. A liquid phase balance of the dissolved species is made around the vessel in order to determine the precipitation rate. The first balance calculated is the total sulfur precipitation in the scrubber.

First, a general liquid phase material balance is made:

$$\text{In} = \text{Out} + \text{Accumulation} \qquad \text{(F-17)}$$

Again assuming steady-state conditions, the accumulation term is zero. Therefore, the sulfur precipitation in the scrubber is described by

$$\sum_{in} \text{T.S. flow(aq)} + \Delta SO_2(g) = \sum_{out} \text{T.S. flow(aq)} + \text{T.S. precipitation} \qquad \text{(F-18)}$$

Which upon rearrangement becomes:

$$\text{T.S. precipitation} = \sum_{in} \text{T.S.(aq)} - \sum_{out} \text{T.S.(aq)} + \Delta SO_2(g) \qquad \text{(F-19)}$$

$$= \frac{22700\ \ell \quad .0114\ \text{gmoles}}{\text{minute} \qquad\quad \ell} - 11100(.0304)$$

$$- 8000(.0249) - 3390(.0277) + 242$$

$$= -130\ \text{gmoles/minute}$$

The negative sign indicates that 130 gmoles per minute of sulfur are dissolving in the scrubber rather than precipitating.

The sulfur precipitation in the draft tube, hold tank, and surge tank are calculated in the same manner. However, they have no $\Delta SO_2(g)$ term.

$$\text{T.S. precipitation} = \sum_{in} \text{T.S.(aq)} - \sum_{out} \text{T.S.(aq)} \qquad \text{(F-20)}$$

$$\text{Draft tube T.S. ppt.} = LBD(TS_{LBD}) + UBD(TS_{UBD}) + SCB(TS_{SCB}) - DTE(TS_{DTE}) \qquad \text{(F-21)}$$

$$= 11100(.0304) + 8000(.0249) + 3390(.0277)$$

$$- 22700(.0112)$$

$$= 376\ \text{gmoles/minute}$$

$$\text{Hold tank T.S. ppt.} = \text{DTE}(\text{TS}_{\text{DTE}}) - \text{HTE}(\text{TS}_{\text{HTE}}) \qquad \text{(F-22)}$$
$$= 22700(.0112) - 22700(.0109)$$
$$= 8 \text{ gmoles/minute}$$

$$\text{Surge tank T.S. ppt.} = \text{HTE}(\text{TS}_{\text{HTE}}) - \text{SCF}(\text{TS}_{\text{SCF}}) \qquad \text{(F-23)}$$
$$= 22700(.0109) - 22700\ (.0114)$$
$$= -12 \text{ gmoles/minute}$$

The total sulfur precipitation rate can now be obtained by adding the values for each vessel.

$$\text{Total sulfur precipitation} = \text{scrubber ppt.} + \text{draft tube ppt.} + \text{hold tank ppt.} + \text{surge tank ppt.}$$
$$= -130 + 376 + 8 - 12 \qquad \text{(F-24)}$$
$$= 242 \text{ gmoles/minute}$$

In a similar manner, the carbonate precipitation can also be calculated by replacing the total sulfur value with the appropriate liquid phase carbonate value. The flow rates remain the same and precipitation rates can be found for three vessels. The total carbonate precipitation rate in the holding system is 40 gmoles per minute. A carbonate precipitation rate for the scrubber can not be calculated because the amount of carbon dioxide sorbed from the flue gas cannot be accurately measured from gas phase data.

Finally, the dissolution rate of calcium hydroxide can be calculated. I.R. scans have shown that no calcium hydroxide is present in the scrubber feed solids. Therefore, all of the $Ca(OH)_2$ solids are dissolved in the holding tanks. The total calcium precipitation in each reaction vessel must be equal to the sum of the $CaSO_3$, $CaSO_4$, $CaCO_3$ and $Ca(OH)_2$ precipitation rates. Since the total sulfur and carbonate precipitation rates have been calculated, the calcium hydroxide dissolution rate can be obtained by difference. First, the total calcium precipitation rate must be calculated. The following general equation can be applied for each vessel:

$$\text{Ca ppt} = \sum_{\text{in}} \text{Ca flow(aq)} - \sum_{\text{out}} \text{Ca flow(aq)} \qquad \text{(F-25)}$$

$$\begin{aligned} \text{Draft tube Ca ppt} &= \text{LBD}(\text{Ca}_{\text{LBD}}) + \text{UBD}(\text{Ca}_{\text{UBD}}) + \text{SCB}(\text{Ca}_{\text{SCB}}) \\ &\quad - \text{DTE}(\text{Ca}_{\text{DTE}}) \qquad \text{(F-26)} \\ &= 11100(.0263) + 8000(.0235) + 3390(.0249) \\ &\quad - 22700(.0179) \\ &= 158 \text{ gmoles/minute} \end{aligned}$$

$$\begin{aligned} \text{Hold tank Ca ppt} &= \text{DTE}(\text{Ca}_{\text{DTE}}) - \text{HTE}(\text{Ca}_{\text{HTE}}) \\ &= 22700(.0179) - 22700(.0178) \qquad \text{(F-27)} \\ &= 2 \text{ gmoles/minute} \end{aligned}$$

$$\begin{aligned} \text{Surge tank Ca ppt} &= \text{HTE}(\text{Ca}_{\text{HTE}}) - \text{SCF}(\text{Ca}_{\text{SCF}}) \\ &= 22700(.0178) - 22700(.0177) \qquad \text{(F-28)} \\ &= 2 \text{ gmoles/minute} \end{aligned}$$

The calcium hydroxide dissolution for each vessel can now be calculated from the following equation:

$$Ca(OH)_2 \text{ diss.} = \text{TS ppt} + CO_3 \text{ ppt} - \text{Ca ppt} \qquad \text{(F-29)}$$

$$\begin{aligned} \text{Draft tube diss.} &= 376 + 31 - 158 \\ &= 249 \text{ gmoles/minute} \end{aligned} \qquad \text{(F-30)}$$

$$\begin{aligned}\text{Hold tank diss.} &= 8 + 6 - 2 \\ &= 12 \text{ gmoles/minute}\end{aligned} \qquad \text{(F-31)}$$

$$\begin{aligned}\text{Surge tank diss.} &= -12 + 3 - 2 \\ &= -11 \text{ gmoles/minute}\end{aligned} \qquad \text{(F-32)}$$

Summing these three values produces a calcium hydroxide dissolution rate of 250 gmoles per minute.

Based on these rate calculations it is apparent that 1) significant dissolution of the calcium sulfite-sulfate solid solution was occurring in the scrubber and 2) most of the solid-liquid mass transfer which was occurring in the reaction tank system was happening in the draft tube.

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(3) Holcombe, L.J., and K.W. Luke, "Characterization of Carbide Lime to Identify Sulfite Oxidation Inhibitors," EPA 600/7-78-176, September, 1978.